EVALUATION OF ADHESION – COHESION OF SOME TBCs USED FOR INTERNAL COMBUSTION ENGINE VALVES USING SCRATCH METHOD

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In this study we analysed using the scratch method, the adhesion and cohesion of three thermal barrier coatings (Cr_2C_3 - Ni20Cr, MgZrO - 35NiCr, ZrO_2 - 5CaO (with Al_2O_3 -30 (Ni20Al) as bonding layer) deposited by thermal spray on the attack surface of some exhaust valve discs, both in the initial state - after deposition and after a certain period of operation. After evaluating the obtained results and the SEM images of the tested surfaces, it was noticed that there are no major destructions, delaminations or partial or total exfoliation of the analysed TB layers, which confirms good cohesion and adhesion to the substrate, as well as preserving the resistance after a certain operating range at high temperatures.

Keywords: adhesion, cohesion, thermal barrier coating (TBC), scratch method.

1. Introduction

The evaluation of the adhesion and cohesion of a coating deposited by thermal spraying to its substrate is very necessary due to the close relationship between these characteristics and the resistance to mechanical stresses, wear and abrasion. Those evaluations can be done by several methods, only a small part of them being standardized. The most commonly used method is to apply traction forces to the ends of two samples bonded one to another, one of them being the coated one. Another method is to apply a force on the cross-section of a coated sample to a threshold that only blocks the coating movement. However, these two methods cannot be successfully used to test thermal spraying coatings because of their specific lamellar structure and also because of the quality and strength of the solder used.

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In the literature, a method of assessing the adhesion and cohesion to the substrate of thermal coatings based on scratch tests was presented [1]. This test method is a comparative method based on the values of the critical forces that produce defects in the deposited layers, in order to evaluate the relative adhesion and cohesion properties to the substrate. It is called the "scratch" test because it is executed by scratching the specimen with a specially designed tip at a predefined load and at a constant speed, depending on the type of analyzed material. This method consists in applying the scratch test on the cross section of a metallographic prepared sample (embedded into the resin, grinded and polished). The indenter must have a linear motion with a constant force. The start point of the scratch is the substrate and the direction is perpendicular on the coating. The final point of the scratch mark must be outside the sample, into the resin. This will result in a conical breaking profile, either in the substrate-coating area (to be interpreted for adhesion evaluation) or in the deposited layer (which will be interpreted for cohesion evaluation) [2].

In this study we examined the adhesion and cohesion of thermal coatings produced by atmospheric plasma spraying on the attack surface of some exhaust valve discs, both in the initial state - after deposition, and after a certain period of operation. Because the coatings analyzed in this study have a thickness between 200-400-μm, we applied the scratch tests for the evaluation of their adhesion and cohesion both longitudinal and on the cross-section. For the best interpretation, the scratch-based recordings are supported by microstructure observations made using electronic microscopy [3 - 5].

2. Materials and methods

The three types of coatings analyzed in the present study were realized using the atmospheric plasma spraying method in normal atmosphere. The deposition substrates were discs of exhaust valves from internal combustion engines. Four types of commercial powders produced by Metco Oerlikon were used to obtain the thermal barrier coatings, as can be seen in Table 1.

Table 1

Powders used to obtain thermal barrier coatings

Sample / Layer	Sample 1 S1	Sample 2 S2	Sample 3 S3
Bonding layer / manufacturer code	Al_2O_3-30(Ni20Al) / 410NS		
Top coat/ manufacturer code	Cr_2C_3 – Ni20Cr / 81NS	MgZrO – 35NiCr / 303NS	ZrO_2 - 5CaO / 201NS

In order to make observations on the quality of the coatings deposited after use in operation, four valves were coated for each type of powder chosen. These

were mounted on a test bench made from a functional engine of Dacia 1400, model 102/13 [6]. Each set was tested in operation as follows:
- day 1: 5 hours of normal high-speed alternating with high speed;
- day 2: 8 hours of operation;
- day 3: 9 operating hours;
- day 4: 8 hours of operation;
- day 5: 6 hours of operation.

From each set of exhaust valves, one sample was taken, and the scratch test was performed.

The tests were carried out using the 2M-CTR UMTR Microtribometer, using an indenter DFH-20 Dual Friction / Load Sensor type, with a tungsten carbide microblade with a tip radius of 0.4 mm. It was chosen the Progressive Load Scratch Test mode (PLST) with a maximum load of 10N and a forward velocity of 0.1mm-/-sec for the scratch test on the sample surface and the Constant Load Scratch Test (CLST) test with a 10N load for scratch cross section (10 mm / min, 30 seconds).

Interpretation of the results was also completed by evaluating the surface morphology on which the scratch tests were performed using the Quanta 200 3D microscope (FEI, The Netherlands, 2009) with the Low Field Detector and Z contrast at various magnification (100x, 300x, 600x, 1000x) and the semi-quantitative elemental chemical analysis module manufactured by EDAX.

3. Results and discussions

According to the literature [1,2], in the case of the evaluation of the adhesion/cohesion of a coating by scratch on cross-section, the following geometry measurements of the cones resulting from the rupture of the coating at its interface with the resin embedding support are made: depth (a), length cone (b), projected cone area (A = (a x b) x 2). The latter is considered to be the most important characteristic comparison factor since it demonstrates a direct proportionality relationship with the load force used in the scratch test.

In the case of the coatings that are the subject of this study, no formation of the breaking cone was observed either at the substrate-coating interface or at interface between the coating and the inclusion resin. For example, we present the resulted areas for samples 2 and 3 in Figs. 1 and 2. It is noted the lamellar structure specific to thermal spraying coatings and the resultant mark of the blade applied with a constant force of 10N on the surfaces of the three materials: steel substrate, TBC and mounting-resin. In the case of used samples, however, a slight breakage of the coating at the interface with the resin is observed, which means that the layer has a lower cohesion when compared to the initial state.

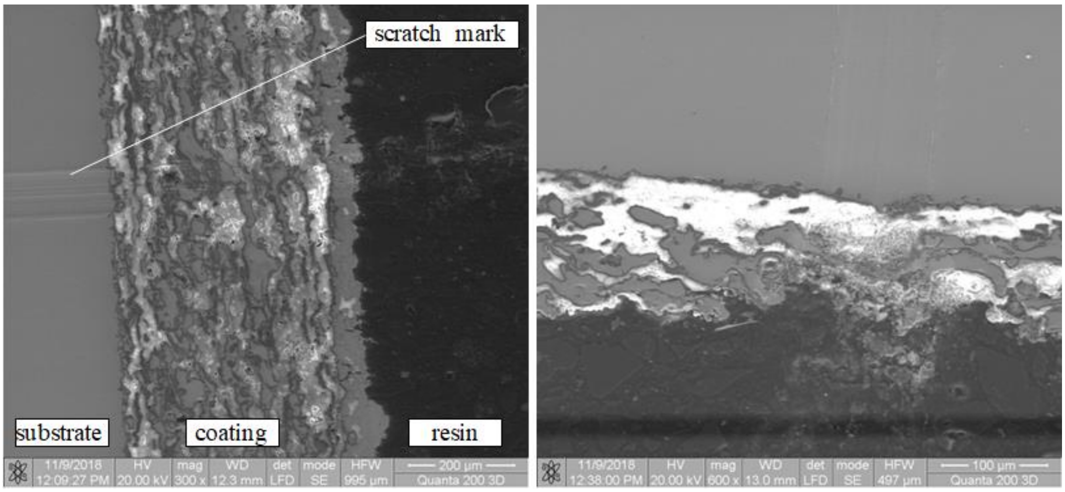


Fig.1. SEM images of the S2 coating on cross section after CLST, comparatively before (a – 300x) and after operation tests (b – 600x)

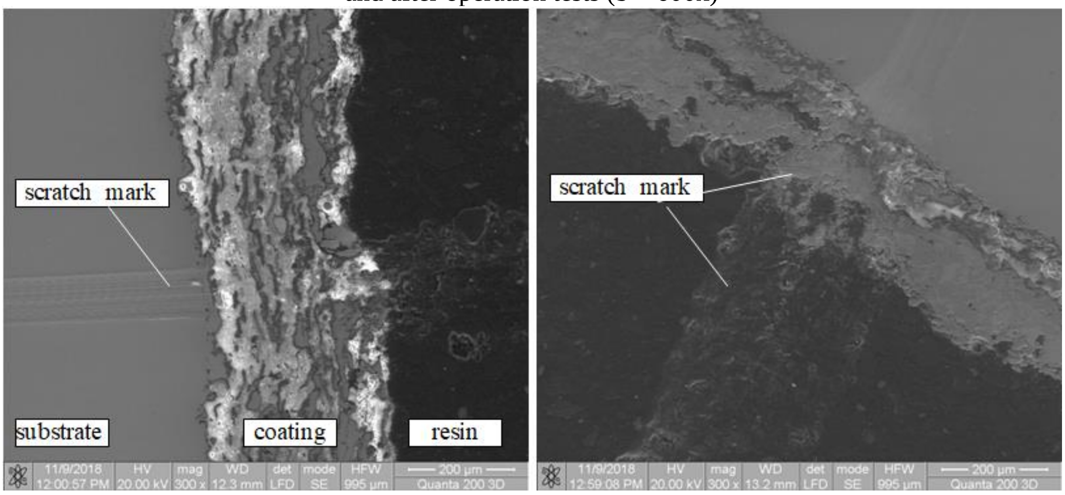


Fig.2. SEM images at magnification of 300x of the S3 coating on cross section after CLST, comparatively before (a) and after operation tests (b)

To help explaining the microstructural aspects observed in Figs. 1 and 2, we also performed a comparative analysis of graphs of the applied and resulting forces from the CLST test. In Fig. 3 are presented the results obtained in case of sample 2. The different behavior caused by the transition from one type of material to the other within the scratch test is visible, the largest friction coefficient (COF) with major fluctuations being the one recorded on the resin. The fact that the same type of major variation is not observed when passing from the steel substrate to the coating gives us valuable clues to the fact that there is a very good adhesion between the two materials.

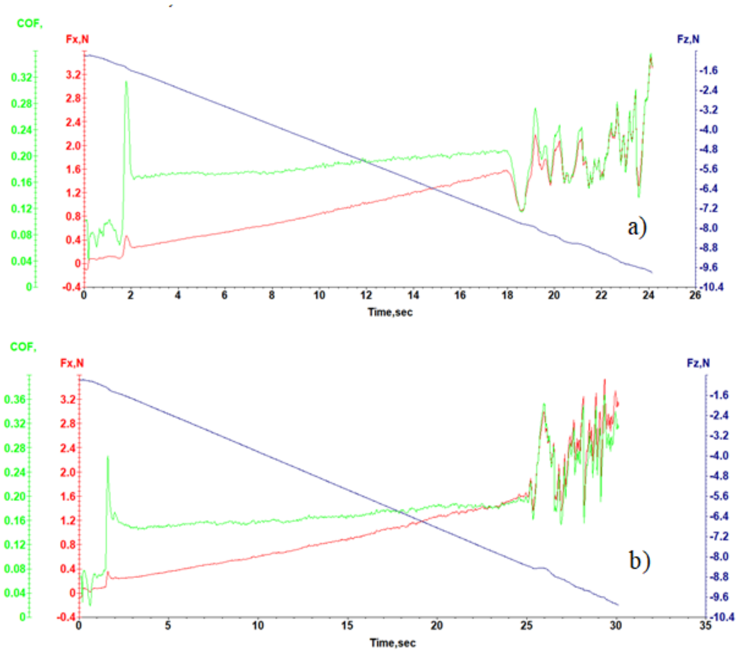
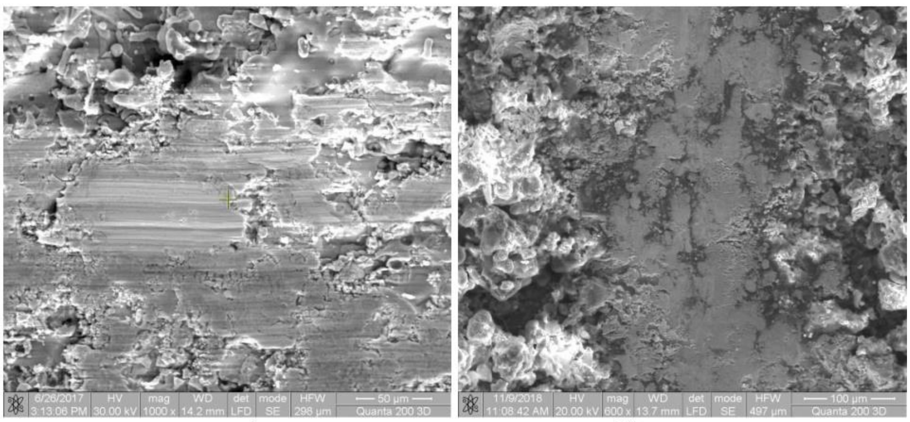
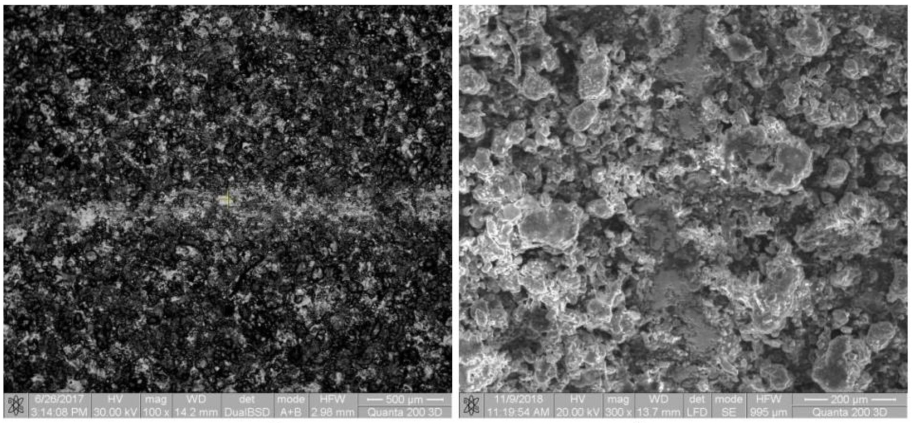


Fig.3. The variation of COF, Fx and Fz forces with the scratch test length on the cross section of sample 2 in initial state (a) and after wear (b)

In this study we also carried out the longitudinal scratch test on the surface of the samples. The morphology of the start / finish regions of the scratch trace results was analyzed and is presented for each of the six samples in Figs. 4, 5, 6. In the case of all the analyzed samples, both in the initial state and those taken from the valves used in the operation of the internal combustion engine, it was observed that the specific structure of the coatings produced by spraying, consists of splashes (the totally or partially melted powder particles pulled to the substrate by the carrier gas jet), micro-cracks and pores of various sizes.

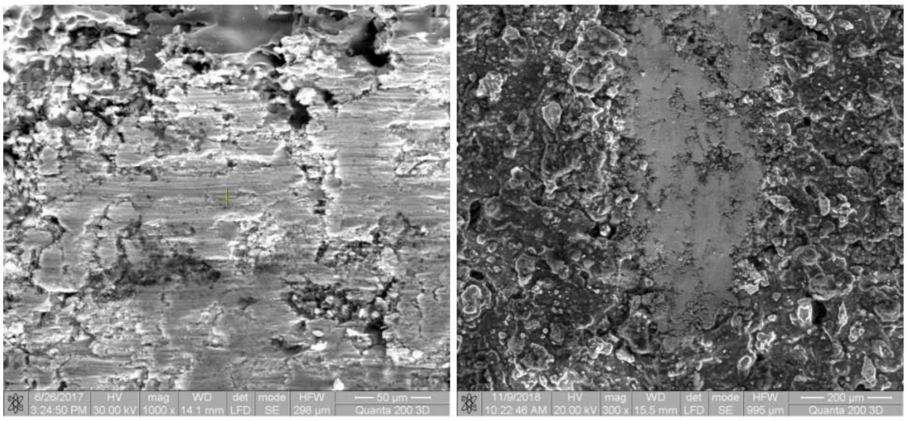


a) b)

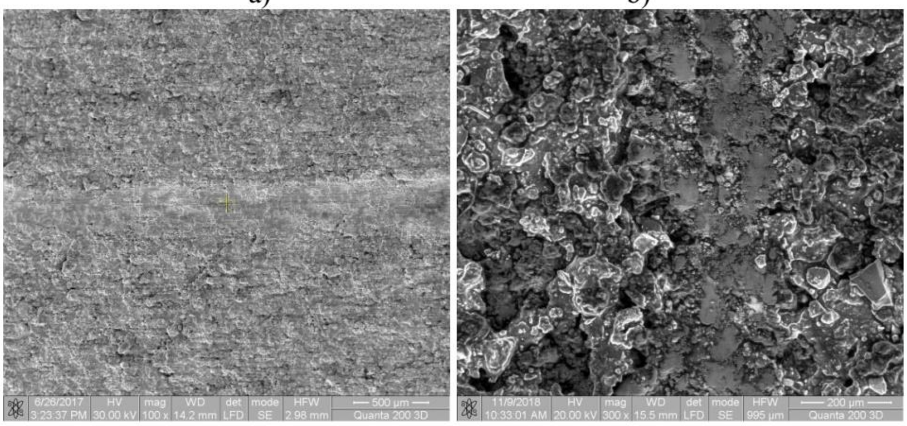


c) d)

Fig. 4. SEM images of the S1 coating, comparatively before and after operation tests, at the final point (a – 1000x, b – 600x) and start point (c – 100x, d – 300x) of the scratch marks.



a) b)



c) d)

Fig.5. SEM images of the S2 coating, comparatively before and after operation tests, at the final point (a – 1000x, b – 300x) and start point (c – 100x, d – 300x) of the scratch marks.

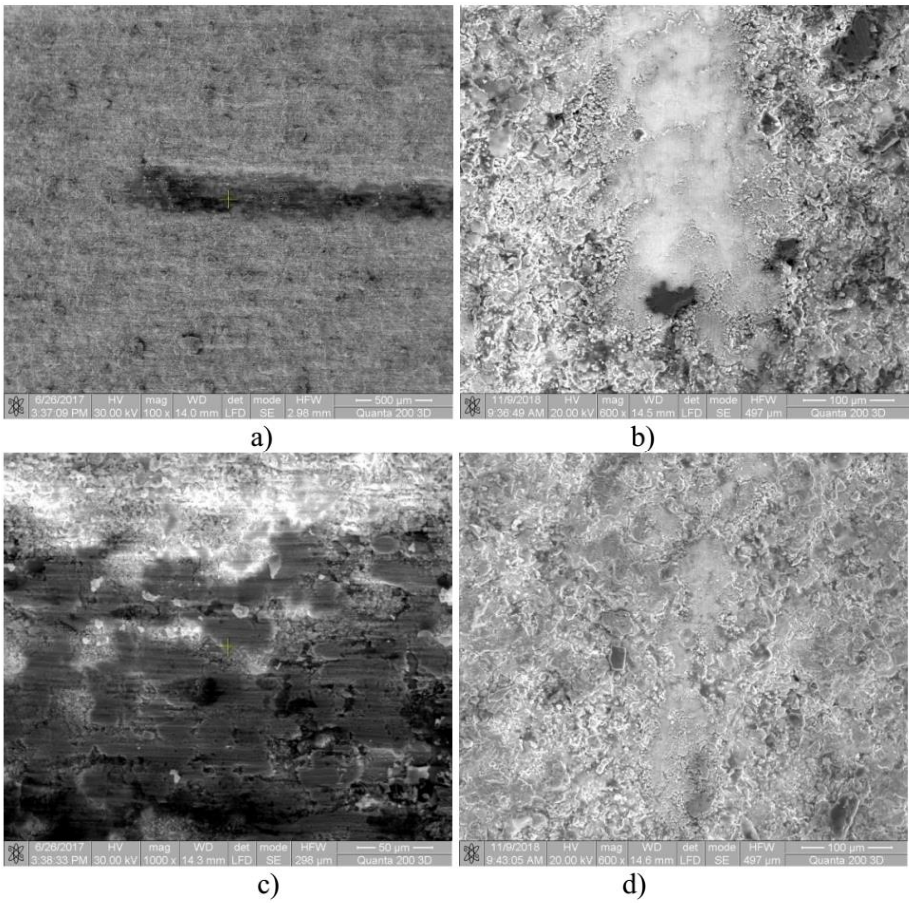


Fig.6. SEM images of the S3 coating, comparatively before and after operation tests, at the final point (a – 100x, b – 600x) and start point (c – 1000x, d – 600x) of the scratch marks

It is noted that at the starting point of the test, where the force begins to increase from 0N, slight traces of plastic deformation of the layer have formed. As the load increases, these traces of plastic deformation become more and more visible, and the scratch mark has a increasing larger width until the test is completed at the maximum load of 10N.

In order to see if the indenter hit the depth of the coating or even produced the exfoliation, we carried out line-level semi-quantitative chemical analysis (EDS - Energy Dispersive Spectroscopy) on the scratch marks because these were the areas subjected to the greatest loads. For example, in Fig. 7, such an analysis is performed on sample 1 after its use in engine operation. Additionally, an EDS analysis of the sample surface was performed in an area adjacent to the scratch mark (Fig. 8) to highlight the presence of the tribofilm produced by combustion during operation and its chemical composition, detailed in Table 2.

As a result of these investigations, it was noticed that within the scratch mark no large variations of the chemical composition appear, which means that the coating has kept its integrity. If exfoliation would have occurred, a very large percentage of Fe in the scratch trace area should have been observed. The only variations observed are those of the Cr and Ni, which were to be expected because the scratch mechanically removed the tribofilm formed by the deposition of the combustion residues during engine operation.

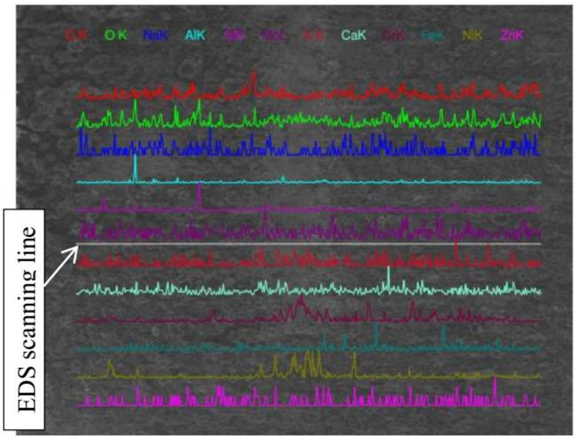


Fig.7. EDS line-map on scratch mark in case of Sample 1 after functioning (80x)

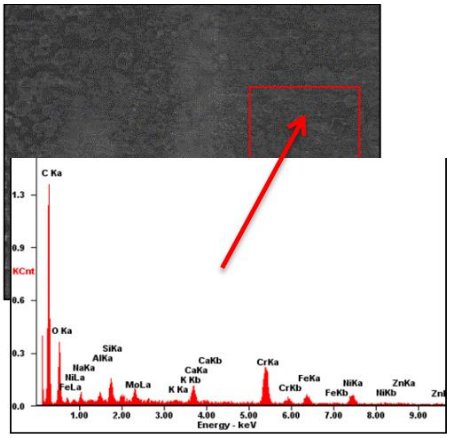


Fig.8. EDS map on Sample 1 surface, near the scratch mark

Table 2

Chemical composition of Sample 1 TBCs in after functioning

Element	C	O	Na	Al	Si	Mo	K	Ca	Cr	Fe	Ni	Zn
Wt%	40.97	16.53	1.95	1.19	3.13	3.13	0.44	3.12	15.07	4.6	7.59	2.27

In none of the cases were observed major breakdowns of the coating, delaminations, partial or complete exfoliation of the TBCs, which gives us clear indications about its resistance to mechanical stresses, and also about the preservation of resistance after a certain period of operation at high temperatures.

4. Conclusions

Assessing the adhesion and cohesion of a layer deposited by thermal spraying on its substrate is difficult to achieve by standardized tests for common coatings because of the specific lamellar structure. For these reasons, a test method was developed based on the scratch tests applied on the cross section of samples on the surface of which various layers were deposited by thermal spraying. This test method is a comparative method based on the values of the critical forces that produce defects in the coatings, in order to evaluate the relative properties of cohesion and adhesion to the substrate.

Based on the results obtained in this study, we can state that the studied coatings show good adhesion to the substrate, both in the initial state after thermal coating and in the worn condition, after the actual use in the operation on an internal combustion engine. Those observations are explained by the fact that there were not observed strength changes during the scratch cross-section test, nor the appearance of the tear-off cone at the substrate-coating interface.

However, slight changes in the scratch mark aspect were observed in the case of sample 2, which means a lower cohesion of this layer compared to the other two.

Elemental semi-quantitative chemical analyzes EDS revealed the presence and quantified the composition of the tribofilm deposited on the valves surfaces as a result of fuel combustion during the internal combustion engine tests.

With the help of the SEM images taken on the surfaces of the samples on which the longitudinal scratch test was performed, it was revealed that, at such mechanical stresses, the coatings retain their integrity. No major breakdowns, delaminations or partial or total exfoliation of the analyzed TBCs were observed, which gives us clear clues about the good cohesion and adhesion to the substrate, their resistance to abrasion and the preservation of resistance after a certain operating interval at high temperatures.

We can say that all types of coatings: Cr_2C_3 - Ni20Cr, MgZrO - 35NiCr, ZrO_2 - 5CaO (with the bonding layer Al_2O_3-30(Ni20Al)) can be used as TBC on internal combustion engine valves.

R E F E R E N C E S

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