

Examination of Internally and Externally Coated Cr_3C_2 Exhaust Pipe of a Diesel Engine via Plasma Spray Method

H. Hazar, S. Sap

Abstract—In this experimental study; internal and external parts of an exhaust pipe were coated with a chromium carbide (Cr_3C_2) material having a thickness of 100 micron by using the plasma spray method. A diesel engine was used as the test engine. Thus, the results of continuing chemical reaction in coated and uncoated exhaust pipes were investigated. Internally and externally coated exhaust pipe was compared with the standard exhaust system. External heat transfer occurring as a result of coating the internal and external parts of the exhaust pipe was reduced and its effects on harmful exhaust emissions were investigated. As a result of the experiments; a remarkable improvement was determined in emission values as a result of delay in cooling of exhaust gases due to the coating.

Keywords—Chromium carbide, diesel engine, exhaust emission, thermal barrier.

I. INTRODUCTION

INTERNAL combustion engines are one of the main reasons of air pollution. The emissions of these engines cause global warming, acid rain, various odors, as well as respiratory and other health problems. The essential reason of these emissions is the factors such as incomplete combustion and nitrogen degradation [1]. In internal combustion engines, parameters such as the surface quality, performance and emission are the components that are directly correlated with each other. Improvement of the surface features positively affects the engine performance and thus, the emission values [2].

One of the systems forming the internal combustion engines is the exhaust system. The coating of the exhaust system enables to both prevent external deformations forming due to its exposure to various solvents in the open field and to meet the negative effect of chemical solvents in the exhaust gas. During the engine start, the engine parts that are continuously in action are exposed to tribological deformations under repetitive strains both in the operating environment (high temperature, pressure, corrosive gases, etc.) and in the speed ranges from low to high. These deformations start from the surface of the material, proceed to its internal structure, and cause damages. Such deformations occurring in the engine parts obstruct the efficient operation of the engine after a while and thus cause increase in fuel consumption and also harmful gas emissions.

H. H. is with the Firat University, Technology Faculty, Automotive Engineering, 23119 Turkey (phone: +90-424-2370000; fax: +90-424-2184674, e-mail: hanbeyhazar@hotmail.com).

S. S. is with the Bingol University, Technical Sciences Vocational Schools, Bingol, Turkey, (phone: +90-426-2160012; e-mail: ssap@bingol.edu.tr).

One of the methods applied to the part to be coated is plasma coating method. Plasma coating method enables the combination of a base metal and a layer having different properties through strengthened surface properties of a layer. Plasma coating also keeps the temperatures of the base metal at a low value during the operation and eliminates the risk of thermal deformation exposure of sensitive parts [3]. Thermal barrier coatings decrease the temperature of the substrate material and protect the material from the negative effects (temperature, corrosion, oxidation) of burnt gases and also corrosion [4].

In this study, internal and external sides of the exhaust pipe of a diesel engine were coated by using plasma spray method. Because the thermal conductivity coefficient of Cr_3C_2 , the coating material, is low, the heat in the exhaust pipe increased. Thus, it was aimed to extend the period of the chemical reaction and to reduce harmful exhaust emissions.

II. MATERIALS AND METHODS

A 4-stroke, single-cylinder, direct injection, air-cooled 6LD 400 model Lombardini branded diesel engine was used as the test engine. In this study, two types of exhaust pipes were used. The first one of these exhaust pipes was a standard exhaust pipe (SP) and the second one was the internally and externally coated exhaust pipe (IECP). Table I shows the technical properties of the engine used.

One of main reasons of selecting the plasma spray coating method is that it does not make any change in the properties of the base material. Internal and external sides of the exhaust pipe were coated with Cr_3C_2 by using the plasma spray method. As the coating material; chromium-based hard coating material Cr_3C_2 was used. The coating applied to internal and external parts was made at an approximate thickness of 100 microns and the protection of the material to be coated from internal and external factors (corrosion, etc.) was also provided. Plasma spray coating method is a thermal spray coating method that is commonly used for making metals corrosion-, oxidation-, abrasion- and heat-resistant by coating them with various powders. Although the properties specified are obtained via the coating performed by this method, toughness and easy formability properties among the superior properties of the base material are also protected. Thus, plasma spray coating enables to gather the outstanding properties of metals and ceramics in a new material. Emission values of SP and IECP were determined and compared. Measurement of exhaust gas temperature (EGT) was taken

from the coated and uncoated 200 cm-long exhaust pipes that are connected to the exhaust manifold. EGT of the exhaust pipes was measured from 6 different areas with 40 cm distance between each of them as of the exhaust manifold. EGT values at 1800, 2100, 2400, 2700, and 3000 rpm were recorded. Table II shows coating production parameters. Fig. 1 shows schematic view of the test mechanism.

Item	Specification
Type of engine	Lombardini 6LD 400
Stroke	4
Number of cylinders	1
Bore/stroke (mm)	86/68
Compression ratio	18:1
Maximum engine power (kW)	6.25 (3600 1/min)
Fuel Type	Diesel
Lubricating	Full pressure
Type of injection	Direct injection
Type of coolant	Air coolant
Max. engine speed (1/min)	3600
Engine volume (mm ³)	382x427x491

Tests were carried out on a Cussons P8160 Model electrical dynamometer. The test mechanism consisted of a test engine, exhaust emission device, thermometer, dynamometer, brake mechanism, fuel tank, and control unit. Fig. 1 shows the test mechanism.

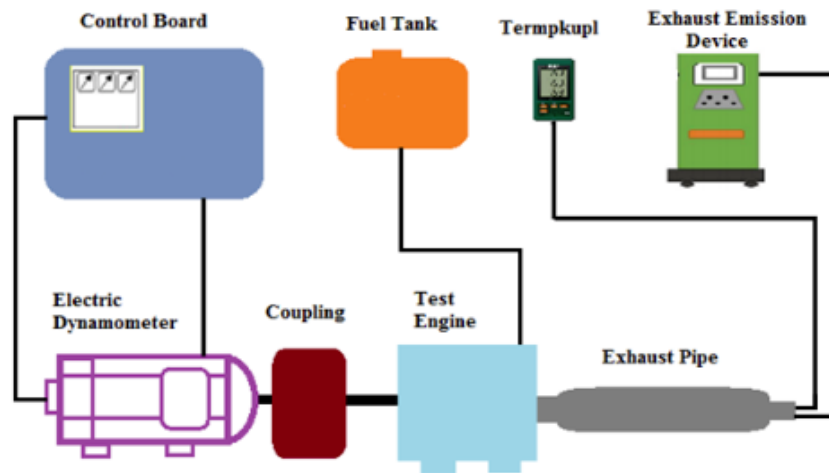


Fig. 1 Schematic view of the engine test mechanism

III. ASSESSMENT OF EXPERIMENTAL RESULTS

A. NO_x Emission

In formation of NO_x emission of the diesel engine, important effects are seen in adiabatic flame temperature, heat release rate and stoichiometric combustion. In diesel engines, pressure, reaction temperature, mixture left from the previous combustion, excess oxygen, ignition delay period and ignition rate are the factors affecting NO_x formation [5]. NO_x generally forms at the temperatures over 1400°C. Especially

the high temperature of the areas, where O₂ is present and the time spent at this temperature are quite effective. N₂ and O₂ quantities in the environment are the factors that are effective on the NO_x formation [6].

Maximum temperatures reached at the diesel engines control the NO formation. At the beginning of the combustion process, the quantity of the burning mixture has an important effect. Because the pressure forming as a result of combustion compresses the unburnt mixture and causes the temperatures increase more, and thus, NO formation also increases [7].

TABLE II
PLASMA SPRAY PRODUCTION PARAMETERS

Parameter	Specification
The Name of Plasma Gun	Sulzer Metco 9 MB
Thickness of Coating (μm)	100
Name of Binding Powder (Ni/Cr)	80/20
Thickness of Binding Powder Layer (μm)	20-30
Argon Pressure (Psig), (l/min)	75
Hydrogen Pressure (Psig), Flow (l/min.)	50
Powder Feed Ratio (gr/min.)	45-60
Spraying Distance (cm)	8.5-9.0
Carrier Gas (N ₂) Pressure (bar), Flow (l/min.), (SCFH)	26

A 6LD 400 model Lombardini branded diesel engine was used in the tests and for the exhaust emission tests, it was operated for approximately 150 hours under actual operating conditions. Diesel engine was connected to the dynamometer (run up area). Then the uncoated SP and the IECF were assembled to the diesel engine, respectively. The test engine was operated at 1800, 2100, 2400, 2700 and 3000 rpm with ½ load and 10 different emission values for every cycle were recorded. For 1800, 2100, 2400, 2700, and 3000 cycles; EGT from six different areas with 40 cm intervals on the exhaust pipe having a length of 200 cm were recorded. The same processes were repeated for the IECF. The results were compared with each other.

These gases, then, are extended in the power stroke and mixed with air or cooler burnt gases and so NO quantity is protected. NO_x quantity changes in direct proportion to the temperature of the combustion chamber. Fig. 2 shows the NO_x emission graphics of coated and uncoated exhaust pipes.

In diesel engines, combustion conditions are improved at middle rpm and the burn-out temperature increases. Thus, NO_x emissions are high between 2500 rpm and 3000 rpm engine cycle interval. If the engine rpm increases more, worsening of the combustion conditions in the area close to maximum engine rpm causes a reduction in mean effective pressure, shortening in the time assigned to combustion and low NO_x emissions. As seen in Fig. 2, the value of NO_x emission at 1800 rpm was lower in SP compared to the value in the coated exhaust pipe (IECP). A linear increase was observed between 1800 rpm and 2700 rpm. At 2700 rpm, NO_x quantity in coated and uncoated exhaust pipes reached to the highest level. Between 2700 rpm and 3000 rpm, the lowest levels were determined in NO_x quantity in coated and uncoated exhaust pipes.

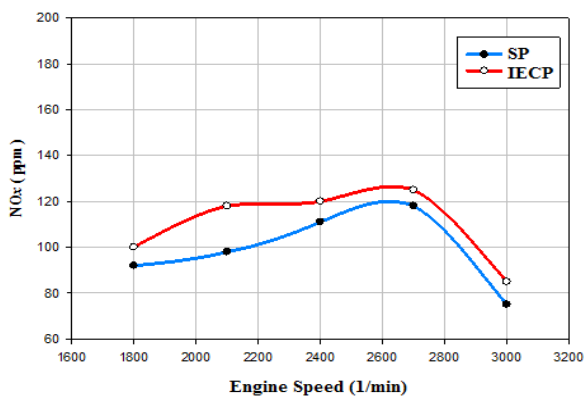


Fig. 2 Change of NO_x emission in SP and IECP

As a result of the tests, it was observed that NO_x emission value in IECP was approximately 10% higher than the NO_x emission value in SP. It was thought that higher NO_x emission in IECP than SP was caused by the thermal barrier applied. Coating of the exhaust line delayed cooling throughout this line and thus, continued the formation of NO_x emission by combining the nitrogen and oxygen molecules in the environment.

B. CO Emission

Air is approximately 21% O₂ and 79% N₂ by volume. Combustion is an exothermic reaction in which the reaction of C and H with O₂ in the intake air gives the products such as H₂O and CO and NO_x in the fuel. This event is also expressed as the oxidation of the fuel. In order to perform the combustion event, the air and fuel taken in the combustion chamber should be mixed at a specific ratio and this ratio is a molar ratio. This expression is used as the stoichiometric ratio and also it is used as the minimum air quantity required for the complete combustion of the fuel [8].

In the combustion reaction, if there is no sufficient O₂, CO forms instead of CO₂ [9]. Among the exhaust gas emissions forming in diesel engines, carbon monoxide (CO) emission is an emission type associated with the parameters such as air-fuel mixture ratio, oxygen quantity and engine temperature. CO forms as a result of the incomplete combustion of petroleum-origin fuels that do not contain oxygen in its molecular structure [10].

As can be understood from Fig. 3, CO value of a diesel engine was higher at lower rpm. The reason is that CO cannot be converted completely into CO₂ due to the low gas temperature in the cylinders at low engine speeds [11].

The lowest CO values in coated and uncoated exhaust pipes were measured between 2400 rpm and 3000 rpm. In the revolutions after 2700 rpm, the absence of sufficient ignition time for combustion prevented the reaction of CO and O₂. Accordingly, CO quantity may increase. It can be asserted that CO emission decreased due to the increase of combustion efficiency at 2700 rpm in average and increased due to the absence of sufficient combustion time at high speeds.

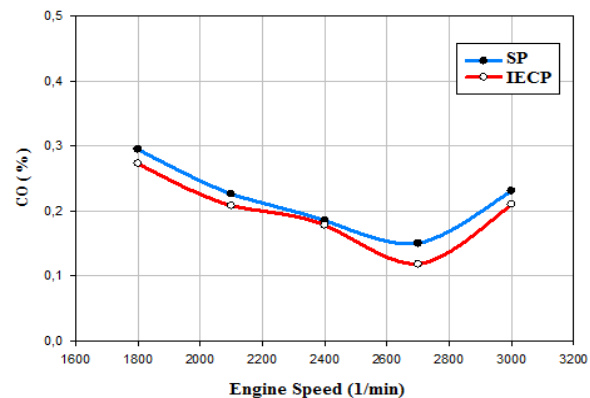


Fig. 3 Change of CO emission in SP and IECP

Because the CO emission is an incomplete combustion product, improvement of incomplete combustion conditions would make contribution to the decrease of CO emission. When evaluated in this respect, incomplete combustion conditions in ceramic coated IECP would be improved. Since time allocated for combustion is longer in IECP, more heat is kept compared to SP. It was thought that higher temperature throughout the exhaust line in IECP compared to SP caused more CO emission to be converted in CO₂ and H₂O. The obtained results support this opinion. Also, it was considered that the short time assigned for the combustion reaction which is the most important factor in the formation of CO emission caused a negative effect in IECP.

As a result of the tests, CO emission value of IECP was averagely 9% lower than SP. While the CO quantity was lower in the exhaust gases in poor and stoichiometric mixtures, CO quantity was high in rich mixtures due to the oxygen insufficiency also in cold exhaust gases. By coating the exhaust pipes with Cr₃C₂, a thermal barrier was provided and it was considered that CO quantity decreased in parallel to

the temperature increase in the exhaust pipes.

C. CO₂ Emission

CO₂ emission is an odorless, colorless, and harmless gas arising in all the normal combustion processes. However, if it exceeds the limit values, it may cause ozone formation and greenhouse effect. When a petroleum-based fuel is exposed to a combustion reaction, i.e., C element in its structure is exposed to oxidation, CO₂ forms as a combustion product. Also, CO₂ emission of a diesel engine is an indicator of the fuel about its efficiency combustion inside the combustion chamber. If a diesel engine operates at low rpm value, its combustion performance is also low because at low rpm values the temperature value in the cylinder is not at optimum conditions, an incomplete combustion occurs [12].

As is seen in Fig. 4, CO₂ emission was at the highest value at 2400 rpm. The reason for this was that the oxygen quantity taken inside the cylinder at maximum moment cycle reached to the highest level. After the maximum moment cycle, the fuel mixture got rich and CO₂ ratio decreased. The emission values supported this. High CO₂ ratio in SP compared to IECP was assessed as normal.

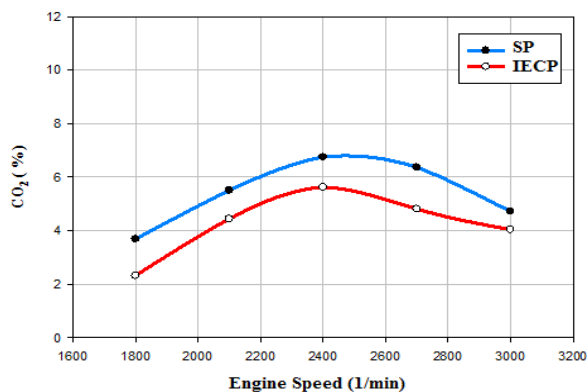


Fig. 4 Change of CO₂ emission in SP and IECP

Because the surface temperature of SP was higher than IECP, higher CO₂ compared to IECP was associated with the emission values of CO₂ and also it was assessed as a result of the chemical reactions throughout the 200 cm exhaust line.

As a result of the tests, an average decrease of 13% was observed in the CO₂ emission value of IECP compared to SP. It was considered that thermal insulation decreased CO₂ emission. It was thought that ceramic coating of exhaust pipes increased the ambient temperature and thus combined the free O₂ molecules in exhaust emission with C atom. Thus, CO₂ emission value of IECP was lower than SP.

D. HC Emission

HC in exhaust gases is an incomplete combustion product. The reason for the increase of HC emissions in diesel engines is the increase of air ratio in the poor mixture and the damping of the fuel in partial areas. Fuel cannot completely combust due to the decrease in the air ratio and the absence of sufficient O₂ and thus, HC ratio increases. Also, during the

atomization of the fuel, drippage of the remaining fuel at the end part of the injector and non-combustion of HC in the molecule cores of the fuel increase the HC ratio [13].

HC emissions in diesel engines generally occur due to the non-completion of combustion. HC molecules with large structures are converted into smaller HC molecules via the effect of temperature. Combustion occurs as a result of the reaction of HC molecules with oxygen. Very rapid combustion reaction and insufficient oxygen cause some small-structure HC compounds not to complete the combustion reaction. These hydrocarbons leave the combustion chamber and release in the atmosphere as a raw gas. During the ID period, poor or rich mixture is seen in some regions [14].

When Fig. 5 was examined, it was observed that HC emissions for the coated exhaust pipes were lower than uncoated exhaust pipes for all rpm values. One of the factors affecting the HC emission is the temperature of the combustion reaction. It can be asserted that low temperature of combustion reaction may be effective on high HC emission for coated and uncoated exhaust pipes at low rpm values. Increase of temperature together with the increasing rpm caused the HC emission to decrease for coated and uncoated exhaust pipes. Also together with the increase in the engine rpm, all the fuel is released outside without combustion due to the low flame speed and thus, HC emissions increase [15].

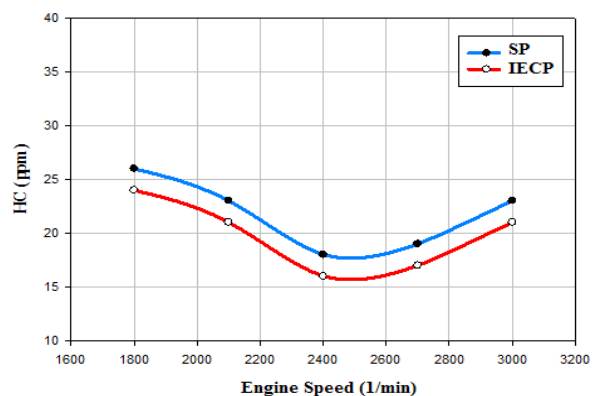


Fig. 5 Change of HC emission in SP and IECP

As a result of the tests, an average decrease of 9% was observed in the HC emission value in IECP compared to SP. During the combustion phase, hydrocarbons that do not participate in the main combustion process are not exactly seen as in the exhaust. After flameout, they are rapidly oxidized in the presence of sufficient oxygen by mixing with burnt gases at high temperature. Thus, HCs form unburnt fuel mixture and partially burnt products. It was considered that the ceramic coating applied reduced this effect in IECP. HCs are oxidized in exhaust system. A ceramic coating with low thermal conductivity coefficient can form a high exhaust temperature. The presence of HCs in this environment for a sufficient period provides HC emission to reduce at a significant level. As a result of coating the exhaust pipes with a material with low thermal conductivity coefficient, HC

emissions were considered to reduce.

E. Smoke (Soot) Density

In diesel engines, smoke forms a major part of the particles forming as a result of combustion. Smoke forms as unburnt carbon particles. These particles essentially contain condensed HC, soot, and inorganic matters [16].

In the diffusion flame forming in diesel engines, the reaction of hydrogen with oxygen is more stable than the reaction with carbon. In this case, the hydrogen molecules in the liquid fuel drop in the cylinder rapidly reacts with oxygen and the remaining carbons cannot burn because of insufficient oxygen and the carbon black particles are released in atmosphere. Smoke is the solid carbon particles formed as a result of these reactions. Because the smoke amount changes as a function of HFK that varies according to the load status of the engine, it is a factor that limits the power of the engine [17].

Smoke formation is generally a phase of diesel combustion. Thus, a large part of the carbon forming at the beginning burns again. However, when excess amount of fuel is sprayed in the combustion chamber in order to increase power, a little smoke is present in the exhaust gases due to insufficient oxygen.

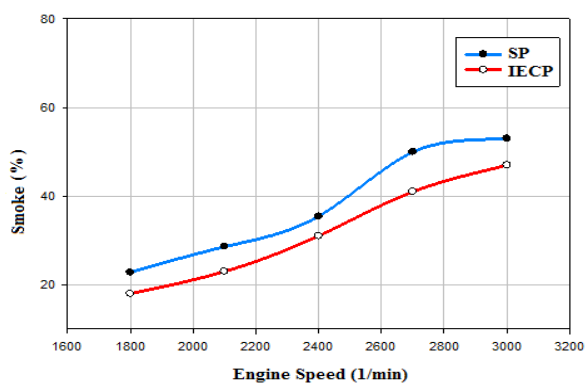


Fig. 6 Change of smoke emission in SP and IECP

When Fig. 6 was examined, it was observed that smoke density at low rpm values was low for the coated and uncoated exhaust pipes. This was caused by the low temperature of combustion chamber and air mobility in the combustion chamber at low rpm values [18].

As a result of the tests, 12% mean decrease is observed in smoke density values of IECP compared to SP. Main function of plasma spray coating is to reduce heat losses and increase thermal efficiency. Owing to the thermal insulation characteristic of plasma spray coating, higher temperatures were obtained in coated exhaust pipes. It was thought that the high temperature occurring in the coated exhaust pipes had a positive effect on smoke density. It can be asserted that the factors such as temperature, reaction time and meeting frequency with oxygen molecules which had a significant effect on smoke formation improved with the applied coating.

G. Comparisons of EGT

During the tests, EGTs of coated and uncoated exhaust

pipes were measured. EGT may change according to the load and rpm in internal combustion engines. As rpm increases, the heat releasing during the combustion increases due to the increase in the fuel amount in the combustion chamber. This situation causes EGT to increase. Measurement of EGT was taken from the coated and uncoated 200 cm long exhaust pipes that are connected to the exhaust manifold. EGTs of the exhaust pipes were measured from six different regions with 40 cm distances between each other. EGT values at 1800 rpm, 2100 rpm, 2400 rpm, 2700 rpm and 3000 rpm were recorded. The regions where EGT was taken were called as the Manifold outlet (MO) Internal EGT, 1st zone External EGT, 2nd zone External EGT, 3rd zone External EGT, 4th zone External EGT and Exhaust outlet (EO) Internal EGT. Graphs of six different zones are seen below.

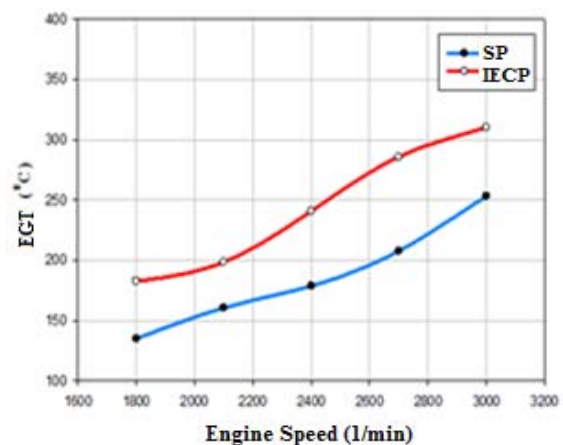


Fig. 7 Manifold outlet (MO) internal EGT

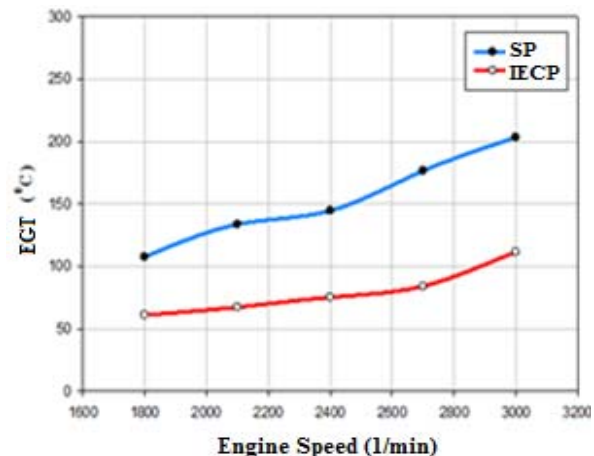
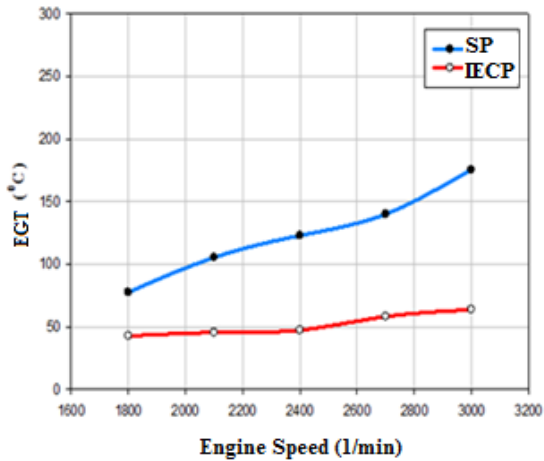
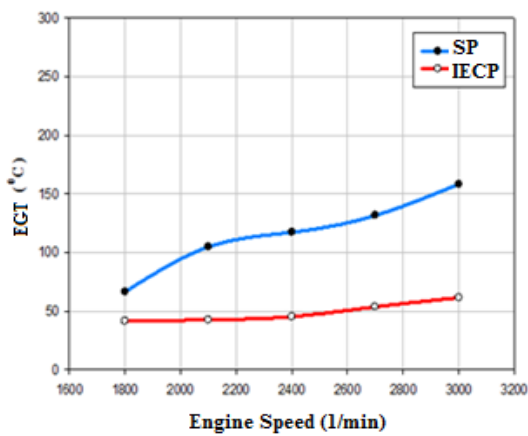
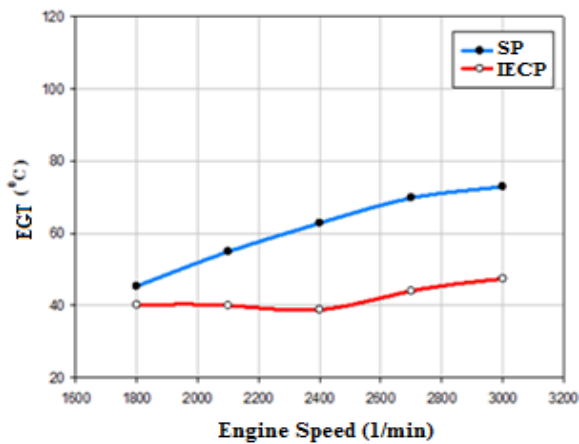


Fig. 8 1st zone EGT

Fig. 9 2nd zone EGTFig. 10 3rd zone EGTFig. 11 4th zone EGT

H. Coating Layer

Fig. 13 shows SEM image of the coating layer taken from the profile of the exhaust pipe. As seen in the figure, it is clearly seen that there is no crack or slit between the coating layer and the base material.

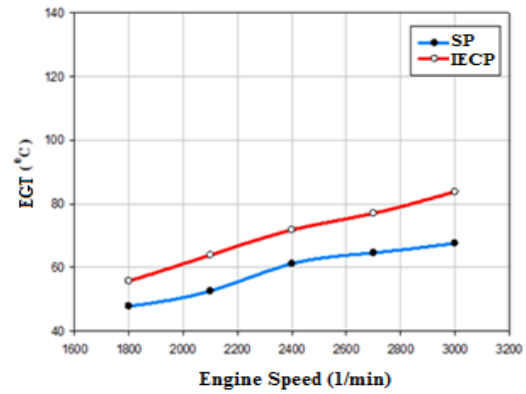


Fig. 12 Exhaust outlet (EO) internal EGT

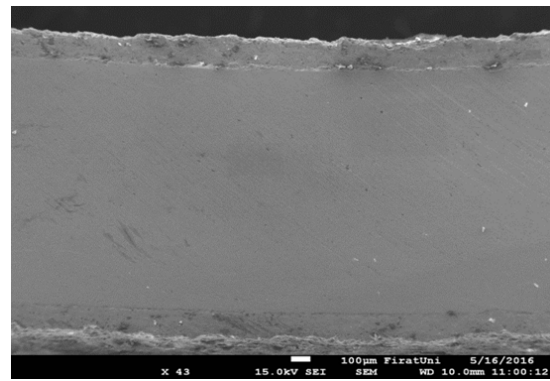


Fig. 13 SEM image of the coating layer of IECP sample

IV. CONCLUSIONS

Internal and external sides of the exhaust pipe were coated with Cr_3C_2 with an approximate thickness of 100 microns by using plasma spray coating method. As a result of this coating applied on the exhaust system, harmful emissions caused by the exhaust gases were decreased. Thus, an environmental-friendly exhaust system was produced. Exhaust tests were performed on a diesel engine. Emissions and EGT values of the exhaust pipes before and after the coating were measured. Then, samples were taken from the same regions of exhaust pipes. Metallographic examinations of these samples (SEM, EDAX, X-RD) were carried out. According to these results:

- ✓ It was observed that NO_x emission value in IECP was averagely 10% higher than the NO_x emission value in SP. It was thought that the reason for this increase was the increase in temperature by a thermal insulation performed in coated exhaust pipes.
- ✓ CO emission value of IECP was averagely 9% lower than SP. It was thought that CO quantity decreased in parallel to the increase of temperature in the exhaust pipes by providing a thermal barrier via coating of the exhaust pipes with Cr_3C_2 .
- ✓ An average decrease of 13% was observed in the CO₂ emission value of IECP compared to SP. It was thought that thermal insulation decreased CO₂ emission.
- ✓ As a result of the tests done after the coating, an average

decrease of 9% was observed in the HC emission value in IECP compared to SP. It was thought that this decrease was associated with thermal insulation.

- ✓ In the smoke density values of IECP, an average decrease of 12% was observed when compared to SP.
- ✓ As a result of EGT tests; it was determined that temperature values of SP were approximately 37% higher than IECP. This showed that coated exhaust pipes were coated with Cr_3C_2 with low thermal conductivity coefficient and a thermal barrier was obtained.

REFERENCES

- [1] B. Aydoğar, *Investigation of NOx emissions in diesel engines fuelled with biodiesel and NOx reduction methods*, Master Thesis, Pamukkale University Graduate School of Natural and Applied Sciences, Denizli, 2008, pp.19-21.
- [2] S. Şap, *The impact of the ceramic coating by plasma spray coating method on the exhaust pipe*, Master Thesis, Firat University Graduate School of Natural and Applied Sciences, Elazığ, 2016, pp.1-2.
- [3] P. K. Aw, A. L. K. Tan, T. P. Tan, J. Ve Qiu, Corrosion resistance of tungsten carbide based cermet coatings deposited by High velocity oxy-fuel spray process, *Journal of Materials Processing Technology*, Warsaw, 2008, pp.5710-5715.
- [4] S. Sharafat, A. Kobayashi, Y. Chan, N. M. Ghoniem, Plasma spraying of micro-composite thermal barrier coatings, *Vacuum* 65 2001, pp.415-425.
- [5] C. Oner, Experimental investigation of the use of a gasoline-powered LPG as fuel and exhaust gas emissions, *Vth National burning symposium*, The book of fire and air pollution reported, Turkey, 2000, pp.228-239.
- [6] A. Ercan, R. Güven, Reduction of NOX emissions in medium speed marine diesel engines, *Vlth International Combustion Symposium*, Turkey, 1999, pp.377-387.
- [7] O. A. Kutlar, M. Ergeneman, H. Arslan, M. Mutlu, *Vehicle Exhaust Pollutants*, Birsen Publishing House, İstanbul, 1998, pp. 13-14.
- [8] C. Sayin, M. Canakci, Effect of injection timing on the engine performance and exhaust emissions of a dual-fuel diesel engine, *Energy Conversion and Management*, Turkey, 2009, pp.203-213.
- [9] E. Önem, P. Sekmen, Determination of lubrication properties of diesel fuels, *Electronic Journal of Vehicle Technology*, Turkey 2009, pp.1 (2): 1-8.
- [10] L. Cherng-Yuan, L. Hsui-An, Diesel Engine Performance and Emission Characteristics of Biodiesel Produced by the Peroxidation Process, *Fuel*, 2006, pp.85: 298-305.
- [11] S. Puhana, N. Vedaramana, B. V. B. Rama, G. Sankarnarayananb and K. Jeychandran, Mahua oil (madhuca indica seed oil) methyl ester as biodiesel-preparation and emission characteristics, *Biomass and Bioenergy*, 2005, pp.28,87-93.
- [12] A. N. Özsezen and M. Çanakçı, Performance and emission analysis of a diesel engine using biodiesel and its mixtures, *Pamukkale University Journal of Engineering Sciences*, 2009, 15 (2): pp.173-180.
- [13] A. Aktaş and Y. Sekmen, Effect of biodiesel-driven diesel engine fuel injection advance on performance and exhaust emissions, *Gazi University Journal of Engineering and Architecture*, Turkey, 2008, 23 (1): pp.199- 206.
- [14] R. Stone, *Motor Vehicle Fuel Economy*, Macmillan Educational Ltd, Houndsmills, 1989.
- [15] H. Hazar and U. Oztürk, The effects of ceramic coating on the performance and emission of hazelnut oil and d2 fuel mixture, *Vth International Advanced Technologies Symposium (IATS'09)*, 2009, pp.13-15 May, Karabük, Turkey.
- [16] A. Demirci, M. Gümüüş, C. Sayın, M. Atmaca, A. K. Binark and M. O. Işıktan, Impact on exhaust emissions of biodiesel-diesel mixtures in a compression-ignited engine, *Vlth International Advanced Technologies Symposium (IATS'11)*, Elazığ, Turkey, 2011, pp.25-27.
- [17] B. Alkaya and A.M. Yıldırım, Methods of reducing vehicle pollutants, *Balıkesir University Faculty of Engineering and Architecture*, Balıkesir, Turkey, 2009 (34): pp.15-20.
- [18] Alkaya, B. ve Yıldırım, A. M., "Taşıt kaynaklı kirleticilerin azaltılma yöntemleri", *Balıkesir Üniversitesi Mühendislik Mimarlık Fakültesi*, Balıkesir, 9 (34): 15-20 (2000).