

Investigation of the Effect of Cr₃C₂ Coating by Plasma Spray Process on Exhaust Pipe of a Diesel Engine

Serhat ŞAP^{1*}, Hanbey HAZAR², Emine ŞAP¹

ABSTRACT: Lifetime of exhaust system decreases rapidly under negative factors such as high exhaust gas temperature, chemical solvents in exhaust gas, water vapor, water in rainy weather, mud, salt poured on the roads to prevent frosting in winter months, etc. Exhaust system of internal combustion engines need to be replaced after a while based on regions and conditions in which they are used. In this study, outer parts of exhaust pipe of a diesel engine were coated with 100-micron-thick chromium carbide (Cr₃C₂) material by using plasma spray method. The effect of chemical and physical solvent and deforming factors that affect externally was examined by coating exhaust pipe with chromium carbide (Cr₃C₂) material. As a result of experiments, it was determined that corrosion resistance increased by 85%. According to scanning electron microscope (SEM), micro hardness, EDAX, and X-RD analyses, the coating was observed to generate a uniform structure on substrate material. Thus, it could be concluded that factors decreasing the lifetime of exhaust system were met by coating material, the surface structure enhanced, and material lifetime increased compared to standard exhaust pipe.

Keywords: Plasma Spray Coating, Chromium Carbide, diesel engines

Plazma Püskürtme İşlemi ile Cr₃C₂ Kaplamanın Dizel Motorun Egzoz Borusu Üzerine Etkilerinin Araştırılması

ÖZET: Egzoz sisteminin ömrü, yüksek egzoz gazı sıcaklığı, egzoz gazındaki kimyasal çözücüler, su buharı, yağışlı havalarda su, çamur, yollarda dökülen tuz, kış aylarında donmayı önlemek için vb. Olumsuz faktörler altında hızla azalır. İçten Yanmalı motorların, kullanıldığı bölgelere ve koşullara bağlı olarak bir süre sonra değiştirilmeleri gerekir. Bu çalışmada, bir dizel motorun egzoz borusunun dış parçaları, plazma sprey yöntemi kullanılarak 100 mikron kalınlığında krom karbür (Cr₃C₂) malzemesi ile kaplandı. Dışarıdan etkileyen kimyasal ve fiziksel çözücünün ve deforme edici faktörlerin etkisi, egzoz borusunun krom karbür (Cr₃C₂) malzemesi ile kaplanmasıyla incelenmiştir. Deneyler sonucunda korozyon direncinin% 85 oranında arttığı belirlenmiştir. Taramalı elektron mikroskobu (SEM), mikro sertlik, EDAX ve X-RD analizlerine göre, kaplamanın ana materyali üzerinde düzgün bir yapı oluşturduğu gözlemlendi. Böylece, egzoz sisteminin ömrünü azaltan faktörlerin kaplama malzemesi ile karşılandığı, yüzey yapısının gelişmiş ve malzeme ömrünün standart egzoz borusuna kıyasla arttığı sonucuna varılabilir.

Anahtar Kelimeler: Plazma Sprey Kaplama, Krom Karbür, Dizel Motorlar

¹ Serhat ŞAP (Orcid ID: 0000-0001-5177-4952), Emine ŞAP (Orcid ID: 0000-0002-7739-0655), Bingöl Üniversitesi, Teknik Bilimler Meslek Yüksekokulu, Elektrik ve Enerji Bölümü, Bingöl, Türkiye

² Hanbey HAZAR (Orcid ID: 0000-0001-7699-0088), Fırat Üniversitesi, Teknoloji Fakültesi, Otomotiv Mühendisliği Bölümü, Elazığ, Türkiye

*Sorumlu Yazar/Corresponding Author: Serhat ŞAP, e-mail: ssap@bingol.edu.tr

* Bu çalışma Serhat ŞAP'ın Yüksek Lisans tezinden üretilmiştir.

INTRODUCTION

The process of accumulating another material on the surface of materials is called as coating. Coating process enables to increase strength of engine parts in harsh working environments, to prevent or minimize their structural deformations, to provide their resistance in corrosive conditions, and to eliminate scratches and wears resulting from mechanical friction (Matthews et al., 2013). Considerable amounts of economic losses occur in machine parts depending on wear and corrosion. It is possible to improve surface properties of materials in order to reduce these losses (Mudgal et al., 2015). One of the methods that can be applied for enhancing the surface quality is plasma spray method. Various techniques are used as coating method. Plasma coating method is one of the methods applied to the part to be coated. Plasma coating method enables a combination of a layer having reinforced surface properties and another layer. It is also possible to repair these parts by coating areas deformed due to wear, heating or corrosion with the help of plasma spray. Plasma coating, also, eliminates risk of precision components to be subjected to temperature strain by keeping base metal temperatures at low during the process (Aw et al., 2008). Elements of engine parts which are continuously in motion while the engine operates are exposed to many deformations. These deformations are observed in working environment (high temperature, pressure, corrosive gases, etc.) and as strains in rpm range from low to high. These deformations start from the surface of the material, move up to its internal structure, and cause damages. These deformations occurring on the engine parts prevent engine to run efficiently after a while, may cause an increase in fuel consumption, and result in harmful gas emissions. Exhaust system is one of the systems composing internal combustion engines. As a result of coating of exhaust system, both external deformations occurring because of exposure to various solvents in an open area will be prevented and negative effect of chemical solvents in exhaust gas will be compensated. Thermal barrier coatings decrease temperature of substrate material and coating material against negative effects of burned gases (temperature, corrosion, oxidation) and wear (Sharafat et al., 2002).

MATERIALS AND METHOD

4-stroke, single-cylinder, direct injection, air cooled 6LD 400 model Lombardini brand diesel engine was used as a test engine. Two types of exhaust pipe were used in this study. While the first one of these exhaust pipes was standard exhaust pipe (SP), the second pipe was the externally coated exhaust pipe (ECP). Table 1 shows technical properties of the engine used. Outer parts of exhaust pipe were coated with chromium carbide by using plasma spray method. The coating process was carried out by a private company. One of the major reasons for choosing plasma spray coating method is that it does not cause any change in properties of base material. Chromium carbide which is a chromium based hard coating material was used as coating material. The coating was applied in approximately 100 micron thickness and it was aimed to protect the coated material from the external factors (corrosion etc.). Plasma spray coating method is a thermal spray coating method widely used in making metals resistant to wear, oxidation, corrosion, and heat by coating them with various powders. The coating performed by this method enabled not only to obtain mentioned properties but also to maintain toughness and formability among superior properties of the base material. Thus, plasma spray coating allows accumulation of superior properties of metals and ceramics in material. Table 2 shows production parameters of coating.

Engine tests were carried out on Cussons P8160 Model electric dynamometer mechanism. Experimental set-up consisted of test engine, exhaust emission device, thermometer, dynamometer, fuel tank, and control unit. Figure 1 shows the experimental set-up. Only the diesel engine was used as a test engine. Samples were taken from the same regions of exhaust pipes. Metallographic examinations

(SEM, EDAX, X-RAY) were performed after these samples were subjected to sanding, polishing, and etching processes. The results were comparatively analyzed. Following these procedures, corrosion tests were performed on coated and uncoated samples.

Table 1. Test Engine specifications

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

Table 2. Production parameters of plasma spray coating

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.)	26

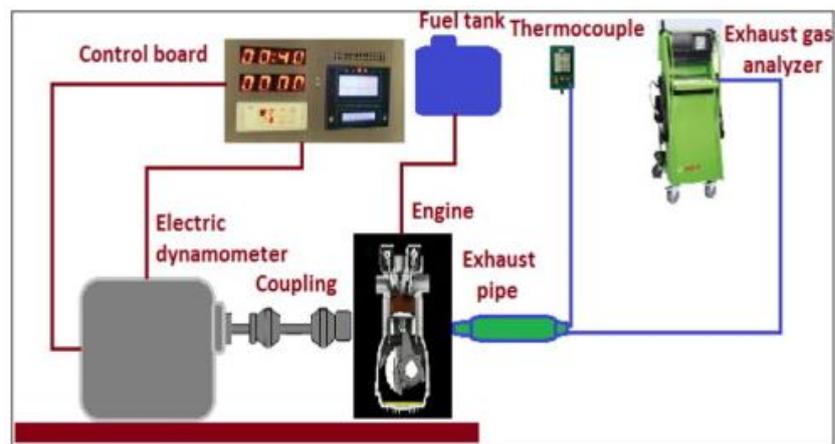


Fig 1. Schematic view of motor test set-up

RESULTS AND DISCUSSION

Microstructure Examination

Micro-hardness measurements

Micro-hardness measurements of coated and uncoated samples were taken under 10 gr/f load. Hardness values of the samples were observed under varying conditions. Stable carbides like Cr₃C₂-WC occurring in coated samples may cause a heterogeneous distribution in hardness (Murthy et al., 2010). Even though Vickers indenter usually came across to coating materials while scanning in hardness analysis, sudden increases may be observed in hardness as a result of pressing the indenter on these carbides. The reason behind why sudden increases and decreases was observed in material surface seen on following hardness-distance graphs below could be interpreted as the fact that Vickers indenter

came across to carbide zone at that moment. As the thickness of coating increases, the material becomes brittle and resistance of the material against impacts decreases. In other words, the material becomes embrittled and brittle.

Figure 2 shows hardness values taken from surfaces of SP and ECP samples towards substrate and diagram of distances from the center of loading point to bakelite.

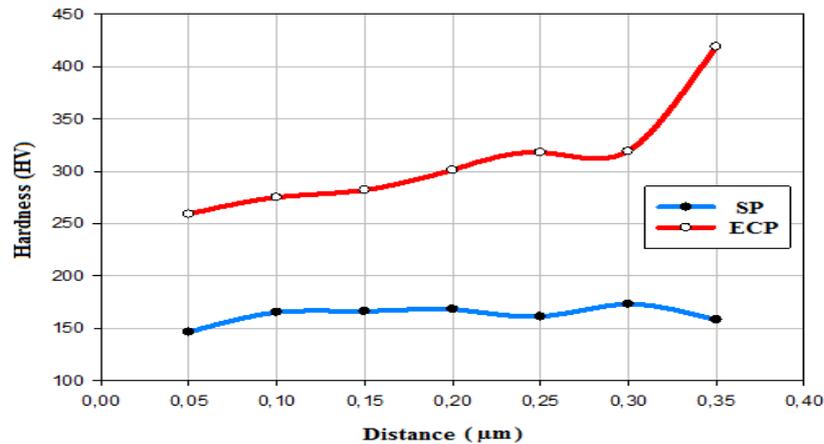


Fig. 2. Hardness-distance change of SP and ECP samples

As seen in Figure 2, hardness values of SP and ECP samples were compared. Here, hardness values taken from 7 regions of SP sample were observed to be close to each other. When literature was reviewed, hardness values of SP sample were determined to be close to hardness values of cast iron. In ECP sample, hardness values linearly increased between 260 HV and 420 HV from coating material to the substrate. Sudden increases and declines could be interpreted as the fact that Vickers indenter came across to carbide zones. Hardness values of ECP sample increased compared to SP sample. This is associated with the fact that ECP sample was coated with Cr_3C_2 material. Hardness is a typical characteristic of Cr_3C_2 material.

Scanning electron microscope (SEM) analysis of samples of exhaust pipes

In detailed microstructure analyses of the coatings, SEM images with 43x, 150x, 350x and 2000x magnifications were taken in order to use for examination of coating morphology and vertical and horizontal crack formations. Figure 3 shows SEM image of ECP sample at 150x magnification.

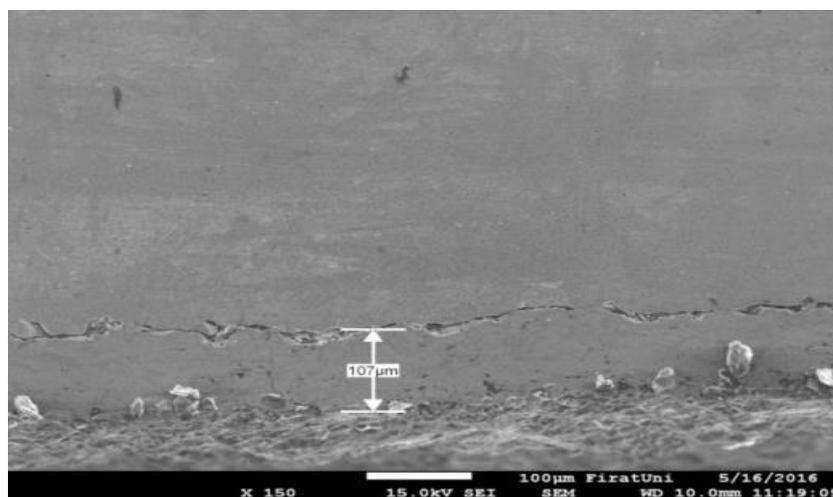


Fig. 3. SEM image of ECP Sample

In Figure 4, thickness of coating was averagely 107 microns in SEM image of ECP sample at 150x magnification. Coating layer, substrate material, and base material were clearly seen. The coating layer was observed to show a good adhesion to base material. Figure 4 shows SEM image of ECP sample at 2000x magnification.

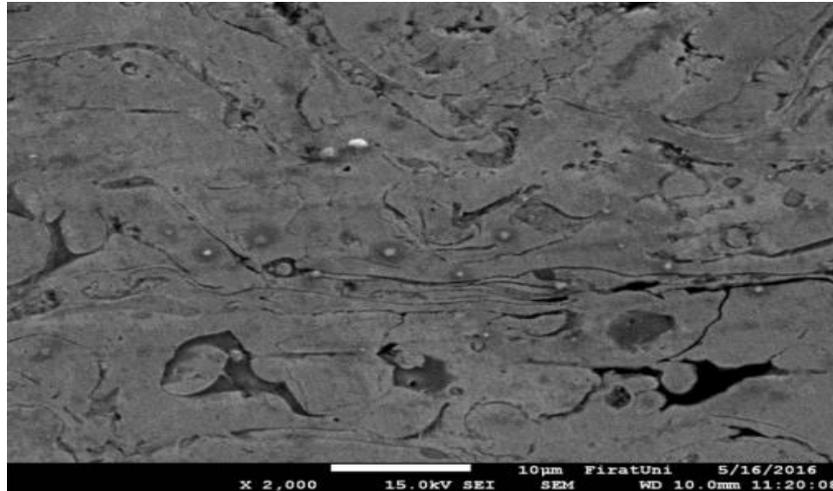


Fig. 4. SEM image of ECP Sample

Cracks occurring in coating layer are clearly seen from SEM image of ECP sample at 2000x magnification in Figure 4. Cracks may occur in plasma spray coatings due to thermal shocks. Pores and voids formed during coating are also observed in SEM image (Suarez et al., 2008). It may be asserted that hardness increased because of excessive carbide in areas where light colored zones were intensive in coating layer (Singh et al., 2018). Figure 5 shows SEM image of SP sample at 350x magnification.

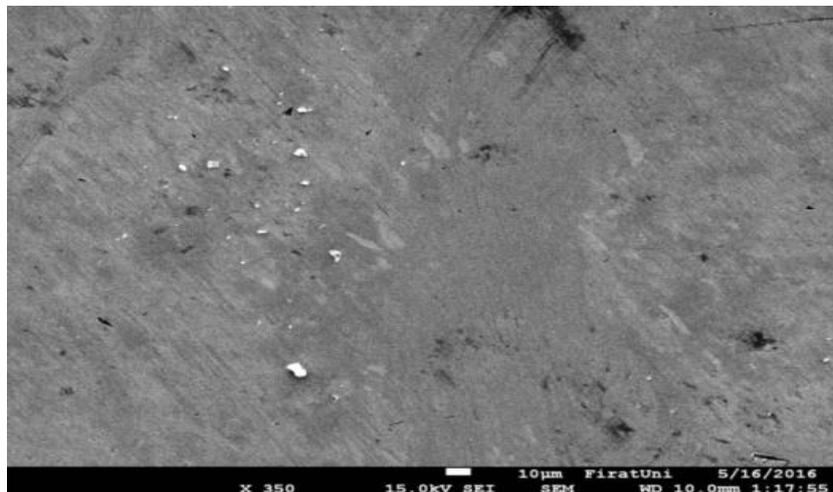


Fig. 5. SEM image of SP Sample

Spherical graphites are seen from SEM image of SP sample at 350x magnification in Figure 5 (Janka et al., 2016). SP sample was not subjected to any coating process. In EDAX analysis of SP sample, it was determined that it contained elements of Fe, C, and Mg. Percentage and atomic weights of these elements were given in EDAX analysis. Figure 6 shows SEM image of SP sample at 2000x magnification.

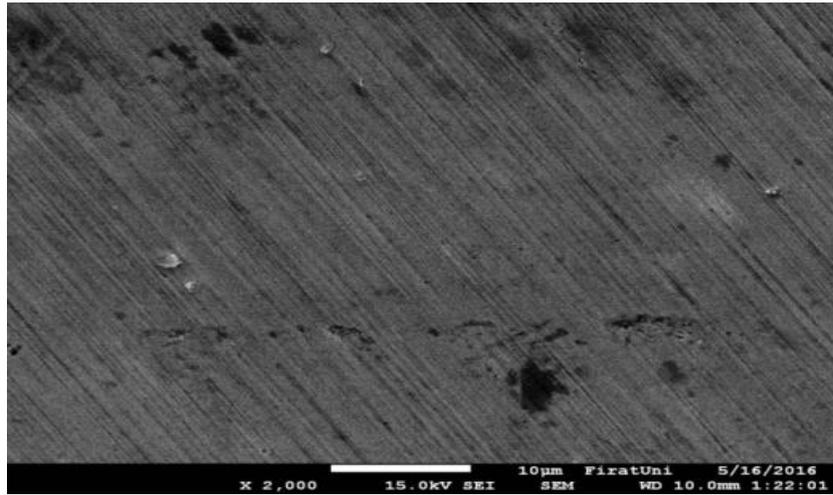


Fig. 6. SEM image of SP Sample

EDAX analysis of samples of exhaust pipes

Figure 7 shows SEM image of ECP sample. In this image, a spot was determined and marked. This spot was named as spectrum 2. EDAX analysis performed in this zone gave us detailed information about the sample. Figure 8 shows elements in zone with spectrum no: 2 in EDAX image of ECP sample. The dominant element was chromium (Cr). Percentage weights of elements determined according to results of analysis made in spectrum 2 zone of ECP sample were 27.70% C , 63.18% Cr, and 9.11% Ni. Their atomic weights were 62.73 C % , 33.05 Cr%, and 4.22% Ni (Hong et al., 2013).

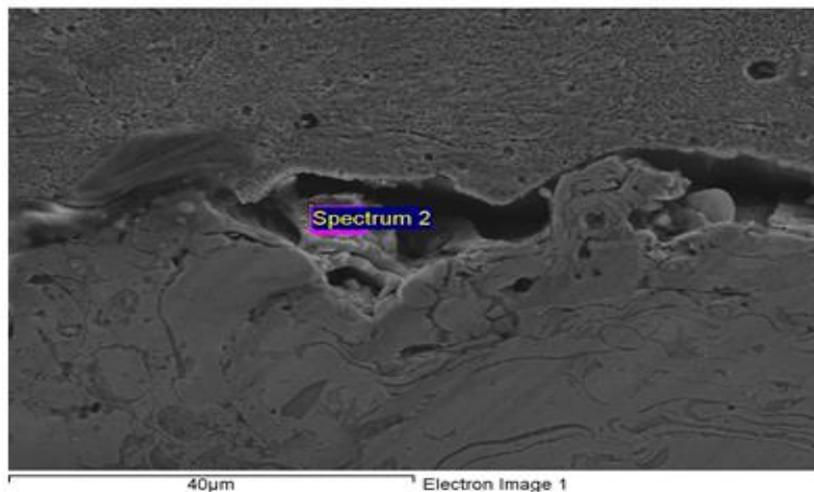


Fig. 7. The point of EDAX Analysis of ECP sample

Figure 9 shows SEM image of SP sample. In this image, a spot was determined and marked. This spot was named as spectrum 1. EDAX analysis performed in this zone gave us detailed information about the sample. Figure 10 shows elements in zone with spectrum no: 1 in EDAX image of SP sample. The dominant element was iron (Fe) (Kamal et al., 2009). Percentage weights of elements determined according to results of analysis made in spectrum 1 zone of SP sample were 17.69 C% , 0.11 % Mg, and 82.20% Fe. Their atomic weights were 49.94% C, 26.60% Mg, and 49.91% Fe.

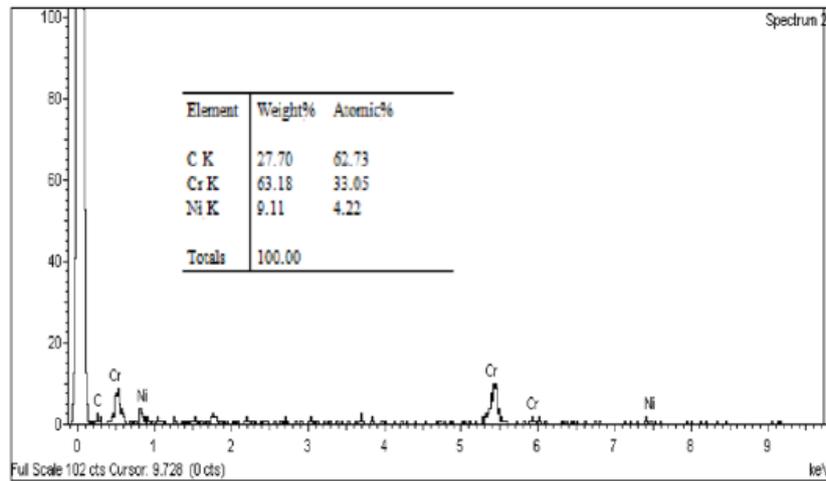


Fig. 8. Graph of EDAX Analysis of ECP spectrum no: 2

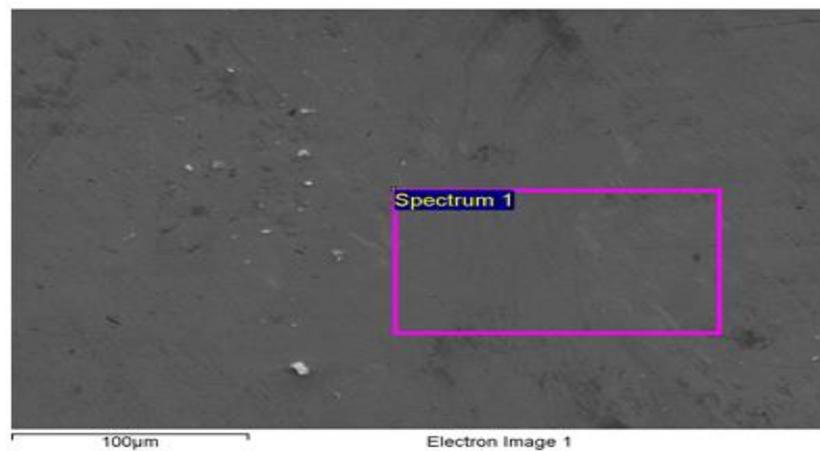


Fig. 9. The point of EDAX Analysis of SP sample

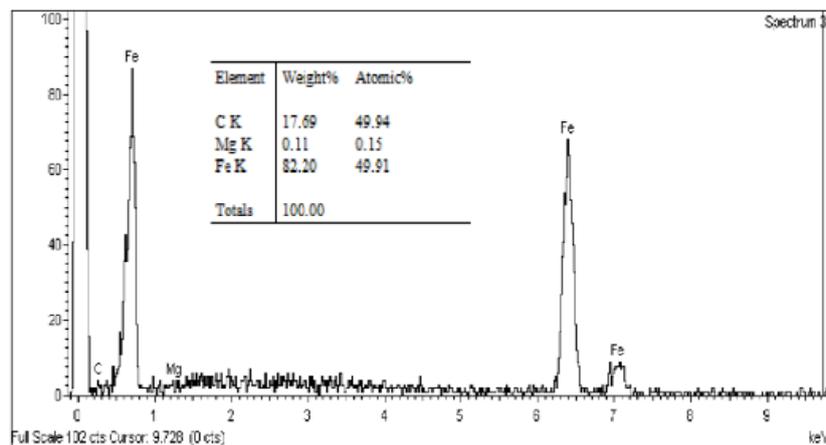


Fig. 10. Graphic of EDAX Analysis of SP spectrum no: 1

X-RD analysis of samples from exhaust pipes

X-ray diffraction analysis was performed in order to determine current phases of coated and uncoated samples. Figure 11 shows the phases found in X-ray analysis of SP sample. These were phases of Fe, C, and Mg. The dominant phases were Fe, C, and Mg because of high peak.

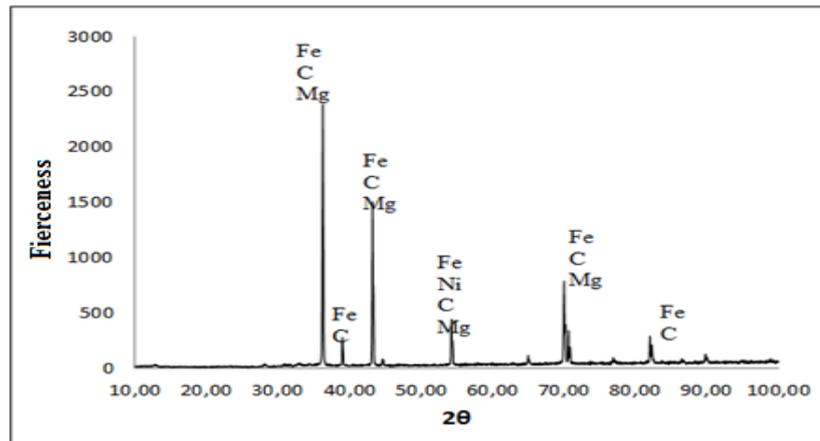


Fig. 11. X-RD Graph of SP sample

Figure 12 shows the phases found in X-ray analysis of ECP sample. These are phases of Ni, C, and Cr. The dominant phases were Ni, C, and Cr because of high peak.

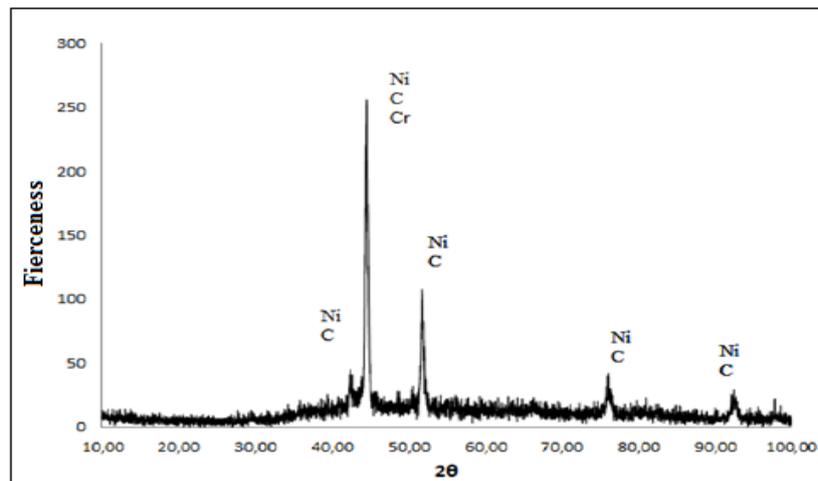


Fig. 12. X-RD Graph of ECP sample

Corrosion Test of Samples of Exhaust Pipes

Two types of corrosion test were applied in this study. The first one of these is determination of corrosion resistance by using Electrochemical Impedance Spectroscopy method; on the other hand, the second one is determination of corrosion current by using Tafel Extrapolation method. Corrosion test was performed by using both methods.

Determination of corrosion resistance by using electrochemical impedance spectroscopy method

Nyquist diagrams taken as a result of electrochemical measurements of exhaust pipe coated with chromium carbide and uncoated exhaust pipe are shown in the graph below. Resistance of the samples against corrosion was determined through nyquist diagrams obtained after samples were soaked in 3.5 % NaCl solution for 1 hour (Zhou et al., 2017). Corrosion resistance of exhaust pipe which was not coated with chromium carbide was measured as 1130 ohm. Corrosion resistance of exhaust pipe coated with chromium carbide was determined to be 8000 ohm. Therefore, corrosion resistance increased by 85 % with coating exhaust pipe with chromium carbide. Corrosion resistance of coated and uncoated samples was determined by using linear polarization method. As a result of this method, corrosion resistance was found to be 84 %.

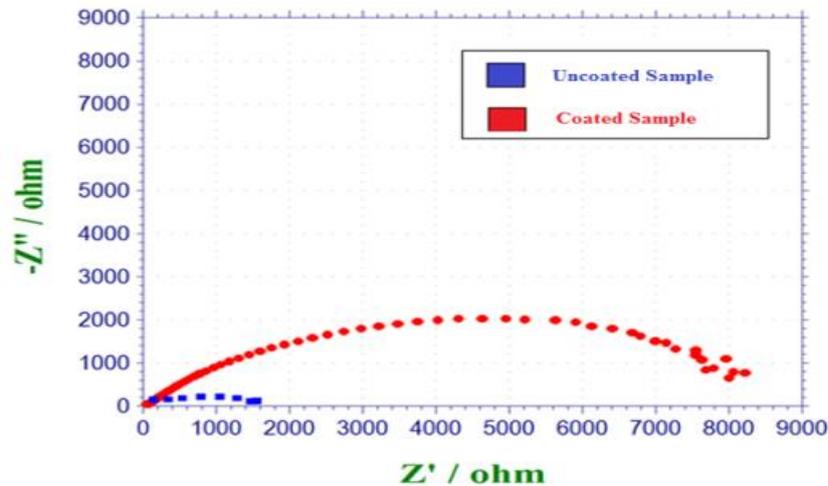


Fig. 13. Nyquist diagrams of coated and uncoated samples

Determination of corrosion current by using extrapolation method

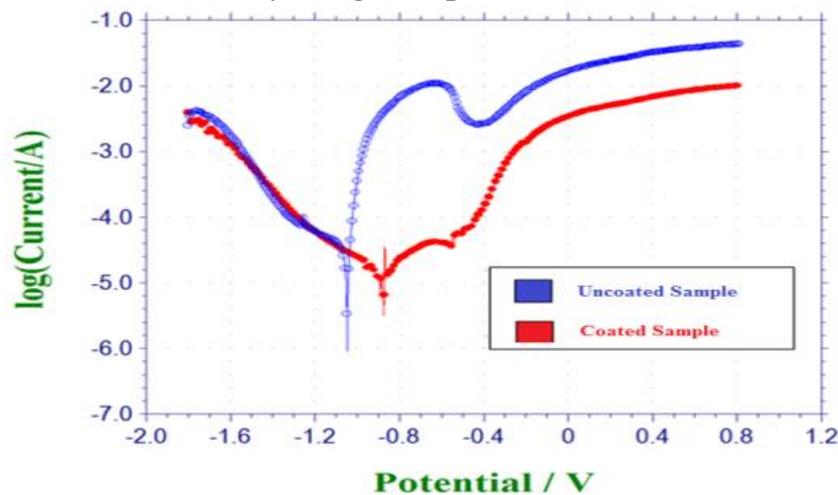


Fig. 14. Semi-logarithmic current-potential graphs of coated and uncoated samples

Semi-logarithmic current-potential graphs of chromium carbide coated and uncoated exhaust pipes were given in the figure above. With the help of curves in the graph, we can get information about corrosion current of the materials. The curve showed in blue belongs to sample that was not coated with chromium carbide and the curve showed in red is semi-logarithmic current-potential curves of chromium carbide coated sample. Corrosion current of coated sample was observed to be lower even though corrosion current of uncoated sample was extremely high. As a result, it could be asserted that corrosion resistance of coated material increased and the current decreased (Nicolaus et al., 2017).

CONCLUSIONS

In this study, exhaust pipe was coated with chromium carbide by using plasma spray coating method in order to make exhaust system more durable. Coated and uncoated exhaust pipes, then, were subjected to exhaust gases by running a diesel engine for about 150 hours. Samples were taken from the same parts of exhaust pipes. Metallographic examinations (SEM, EDAX, X-RD) of these samples were carried out. Micro-hardness and corrosion tests were conducted on coated and uncoated samples following these processes. According to these results;

- ✓ The effect of chemical and physical solvents and deforming factors will be reduced by coating exhaust pipe with chromium carbide (Cr₃C₂). Thus, factors decreasing lifetime of exhaust pipe are compensated by coating material.
- ✓ As a result of corrosion test, corrosion resistance of coated exhaust pipe was found to be 85% higher compared to uncoated exhaust. The corrosion test revealed that lifetime of exhaust pipe material increased.
- ✓ Because chosen coating material had high corrosion resistance, corrosive deformation to occur on exhaust pipe due to environmental conditions was prevented. Strength against high thermal shocks was obtained thanks to homogenous layer formed on the surface, a linear heat distribution was also ensured owing to uniform coating layer existing on surface of exhaust pipe.

ACKNOWLEDGEMENT

The authors would like to thank Firat University (FUBAP –Project No:TEKF.14.11) for his support.

REFERENCES

- Aw PK, Tan ALK, Tan TP, Qiu J, 2008, Corrosion resistance of tungsten carbide based cermet coatings deposited by High Velocity Oxy-Fuel spray process, *Thin Solid Films*, 516, 5710–5715.
- Hong S, Wu Y, Wang Q, Ying G, Li G, Gao W, Wang B, Guo W, 2013, Microstructure and cavitation–silt erosion behavior of high-velocity oxygen–fuel (HVOF) sprayed Cr₃C₂–NiCr coating, *Surface and Coatings Technology*, 225, 85–91.
- Janka L, Norpoth J, Eicher S, Ripoll MR, Vuoristo P, 2016, Improving the toughness of thermally sprayed Cr₃C₂–NiCr hardmetal coatings by laser post-treatment, *Materials & Design*, 98, 135–142.
- Kamal S, Jayaganthan R, Prakash S, 2009, High temperature oxidation studies of detonation-gun-sprayed Cr₃C₂–NiCr coating on Fe- and Ni-based superalloys in air under cyclic condition at 900 °C, *Journal of Alloys and Compounds*, 472, 378–389.
- Matthews S, James B, Hyland M, 2013, High temperature erosion–oxidation of Cr₃C₂–NiCr thermal spray coatings under simulated turbine conditions, *Corrosion Science*, 70, 203–211.
- Mudgal D, Singh S, Prakash S, J, 2015, Hot Corrosion Behavior of Bare, Cr₃C₂–(NiCr) and Cr₃C₂–(NiCr) + 0.2wt.%Zr Coated SuperNi 718 at 900 °C, *Journal of Materials Engineering and Performance*, 24, 1–15.
- Murthy JKN, Prasad KS, Gopinath K, Venkataraman B, 2010, Characterisation of HVOF sprayed Cr₃C₂–50(Ni20Cr) coating and the influence of binder properties on solid particle erosion behavior, *Surface and Coatings Technology*, 204, 3975–3985.
- Nicolaus M, Möhwald K, Maier HJ, 2017, A Combined Brazing and Aluminizing Process for Repairing Turbine Blades by Thermal Spraying Using the Coating System NiCrSi/NiCoCrAlY/Al, *Journal of Thermal Spray Technology*, 26, 1659–1668.
- Sharafat S, Kobayashi A, Chan Y, Ghoniem NM, 2002, Plasma spraying of micro-composite thermal barrier coatings, *Vacuum* 65, 415–425.
- Singh B, Singh G, Sidhu BS, 2018, Analysis of Corrosion Behavior and Surface Properties of Plasma-Sprayed HA/Ta Coating on CoCr Alloy, *Journal of Thermal Spray Technology*, 27, 1428–1435.
- Suarez M, Bellayer S, Traisnel M, Gonzalez W, Chicot D, Lesage J, Puchi-Cabrera ES, Staia MH, 2008, Corrosion behavior of Cr₃C₂–NiCr vacuum plasma sprayed coatings, *Surface and Coatings Technology*, 202, 4566–4571.
- Zhou W, Zhou K, Deng C, Zeng K, Li Y, 2017, Hot corrosion behaviour of HVOF-sprayed Cr₃C₂–NiCrMoNbAl coating, *Surface and Coatings Technology*, 309, 849–859.