Investigation of the Effect of Cr$_3$C$_2$ Coating by Plasma Spray Process on Exhaust Pipe of a Diesel Engine

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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 (Cr$_3$C$_2$) 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 (Cr$_3$C$_2$) 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

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 değiştirilmesi gerekir. Bu çalışmada, bir dizel motorun egzoz borusunun dış parçalarını, plazma sprey yöntemi kullanarak 100 mikron kalınlığında krom karbür (Cr$_3$C$_2$) malzemesi ile kaplanmıştır. Dışarıdan etkileyen kimyasal ve fiziksel çözücüün ve deform edici faktörlerin etkisi, egzoz borusunun krom karbür (Cr$_3$C$_2$) malzemesi ile kaplanmasıyla incelenmiştir. Deneyler sonucunda korozyon direncinin% 85 oranında arttığı belirlenmiştir. Tarama loptik mikroskob (SEM), mikro sertlik, EDAX ve X-RD analizlerine göre, kaplanmanın ana materyal üzerinde düzgün bir yapı oluşturduğu gözlandı. Böylece, egzoz sistemünün ömrünü azaltan faktörlerin kaplama malzemesi ile karşılanlığı, yüzey yapısının gelişmiş ve malzeme ömrünün standart egzoz borusuna kıyasla arttığı sonucuna varılabilir.

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

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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 coatings enable 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 to 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 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 (mm³)         | 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 (N₂) Pressure (bar), Flow (l/min.) | 26                          |

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](image)

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$_3$C$_2$ material. Hardness is a typical characteristic of Cr$_3$C$_2$ 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.
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](image)

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](image)

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.
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).

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.
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.
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.

**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 %.
Determination of corrosion current by using extrapolation method

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 (Cr$_3$C$_2$). 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.

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