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TRIBOLOGICAL BEHAVIOUR AND CORROSION IMPROVEMENT OF THE CHROMIUM COATED PISTON RINGS BY GRAPHENE OXIDE

Doğuş ÖZKAN[1], Yaman ERARSLAN[2], Cem KINCAL[3], Egemen SULUKAN[1]

[1]National Defense University, Turkish Naval Academy, Turkey, dozkan@dho.edu.tr/esulukan@dho.edu.tr
[2]Yıldız Technical University, Turkey, erarslan@yildiz.edu.tr
[3]Istanbul Technical University, Turkey, kincal@itu.edu.tr

Abstract: *Corrosion and wear protection of metal surfaces is an important phenomenon in industrial applications in order to prevent material losses from the surfaces. Graphene is a material which synthesized from the graphite or growth via chemical vapor deposition (CVD) as a single layer of carbon atoms with hexagonal lattice structure and sp2 covalent bonding. Graphene oxide (GO) is one form of the graphene-based materials and is highly promising for corrosion inhibition. To date, corrosion protection of this material has been widely investigated as a sheet on copper or nickel surface. However, to the best of our knowledge, anti-wear reduction of this material has not been investigated especially under lubricated condition. In this paper, chromium coated piston ring was coated GO by CVD at ambient pressure furnace. Optical microscope, scanning electron microscope (SEM/EDX), atomic force microscope (AFM) and Raman analysis were used to characterize the GO coatings. Corrosion resistance of the coatings was evaluated by SP-150 potentiostat galvanostat with 0.5 and 1 M sulphuric acid solutions and wear behaviour of the coating was evaluated by tribometer tests under lubricated condition. Results showed that GO significantly reduced the corrosion rate of ring at extreme corrosive media when compared to chromium ring. Furthermore, GO reacted with ZDDP and form tribofilm to provide wear resistance to ring, which resulted in very effective wear protection because of no wear scar observation on the ring surface.*

Keywords: *Graphene oxide, corrosion inhibition, piston rings coatings, tribofilm, ZDDP.*

1. INTRODUCTION

Piston rings used in internal combustion engines are one of the important application fields of coatings [1, 2]. Chromium (Cr)/chromium nitride (CrN), phosphate (P), diamond-like carbon (DLC) are the coating types and thanks to its good wear and corrosion resistance, Cr is the most commonly used one [3, 4]. Especially, top rings which run at higher pressures and thermal stress due to the combustion process are coated with Cr by physical vapor deposition (PVD) [5, 6]. Cr coating provides wear and corrosion resistance to ring that slides against cylinder liner under boundary lubricating and corrosive conditions due to high contact pressures versus low speed and combustion residues of fuels, respectively [7, 8]. Over the last few years, due to its good hydrophobic structure, graphene oxide (GO) has been investigated to be a corrosion resistant coating by many researches [9-12]. In this study, corrosion resistance and tribological behaviour of CVD grown GO on Cr coated steel piston ring was investigated by corrosion and tribometer tests. Results showed that GO coated piston ring introduced superior corrosion and wear resistance than Cr coated piston ring.

2. MATERIALS AND METHODS

Corrosion resistance of the Cr and GO coated steel rings were evaluated via electrochemistry method. Tribological performance of the coatings was carried out with tribometer tests under lubricated condition. Microscopic and spectroscopic methods were used to characterize tribochemical and morphological changes.

2.1 Sample Preparation and Coating Process

Grey cast iron cylinder liner samples (9.5 mm x 12 mm x 8 mm) were used to counter surface for Cr and GO coated rings with the typical composition of % 93.95 Fe, % 3 C, % 0.3 P, % 0.15 V, % 0.6 Mn, % 2 Si in weight, 270 HV microhardness, and root mean square surface roughness of (Rq) 353.8 nm. Cr ring samples cut from the piston ring in 15 mm length and they had approximately 100 µm coating thickness with Rq=62.4 nm. The hardness of the coatings was measured to be 16 GPa and elastic modulus of the Cr ring was 275 GPa. Cr ring coated with graphene oxide under continuous Ar, H_2 flow in ambient pressure CVD set up. Graphene oxide growth was triggered by the letting of CH_4 into the tube with a rate of 10 sccm for 20 minutes.

2.2 Characterization of GO coating

Optical microscope (Nikon LV-150), SEM-EDX (Zeiss ultra plus Fe-SEM equipped with Bruker XFlash 5010 EDX detector with 123 eV resolution), AFM (Nanosurf Flex-5), and Raman (Renishaw Invia, equipped with 532 nm laser) were used to morphological and chemical characterization of the GO.

2.3 Corrosion and tribometer test conditions

A commercial tribometer was used to friction and wear performance characterization under boundary lubrication condition using fully formulated SAE 5W40 grade lubricating oil. 60 N normal force was applied to sample surfaces and sliding distance was 72.6 meters with 0.055 m/s sliding speed, respectively.

The maximum contact pressures were calculated using elliptical Hertzian contact theory (see Eq. 1).

$$P_{max} = \frac{L}{a.b} \tag{1}$$

The minimum film thickness and lambda ratio for boundary lubricating condition were calculated by Eq. 2 and 3, respectively.

$$h_{min} = 3.63x \frac{(\alpha.E')^{0.49} \left(\frac{\eta_0 U}{E'}\right)^{0.68}}{(W/E')^{0.073}} (1 - e^{-0.68k} \tag{2}$$

$$\lambda_{min} = \frac{h_{min}}{(R_{qb}^2 + R_{qs}^2)^{1/2}} \tag{3}$$

The calculated maximum Hertzian contact pressure of the Cr and GO coatings was 0.19 GPa. In addition, the calculated minimum film thickness of the coatings was 63.30 and the lambda ratios were 0.18. Quantitative determination of the corrosion rates was evaluated via Tafel curve analysis. Corrosion rates were extracted by plotting the logarithm of the current density (I) vs. the electrode potential (V) from the Tafel plots. Corrosion rates (CR) were evaluated by Eq. 4.

$$CR = \frac{I_{corr} xKxEW}{\rho xA}, \text{(mm/year)} \tag{4}$$

3. RESULTS

Fig. 1 shows a morphological and chemical analysis of the coatings by an optical microscope and Raman analysis. Blue oxidized surface was observed with an optical microscope (see Fig. 1(a)) and Raman analysis confirmed GO coating on the Cr surface with the D peak showing disorders at 1350 cm-1, G peak at 1583 cm^{-1} (assigned to the E2g phonon vibrational mode of C sp2 atoms) and 2D peak at 2702 cm^{-1} (see Fig. 1 (b)) [13-15]. In addition, weak CrO peak was detected at 660 cm^{-1} in Raman spectra.

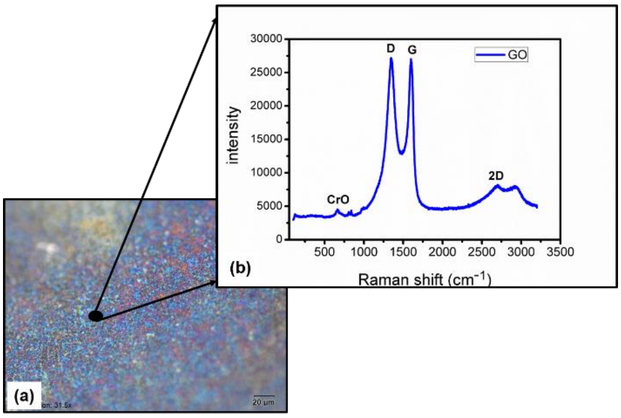

Figure 1. Microscopic and spectroscopic analysis of the GO coating (a) optical microscope analysis, (b) Raman analysis

Table 1 shows corrosion test results and for the 0.5 M solution Cr coating had 6.19 mm/year corrosion rate with 78.73 $\mu A/cm^2$ corrosion current (i_{corr}) while GO coating had 0.11 mm/year CR and 1.41 $\mu A/cm^2$ i_{corr}. When looking at the 1 M solution results, CR of GO was 0.16 mm/year with 2.11 $\mu A/cm^2$ i_{corr} and CR of Cr coating increased to 7.84 mm/year with 99.69 $\mu A/cm^2$ i_{corr}.

Table 1. Corrosion test results of the Cr and GO coated rings

	0,5 M H_2SO_4		**1 M H_2SO_4**	
	Cr Coated Ring	**GO Coated Ring**	**Cr Coated Ring**	**GO Coated Ring**
E_{corr} (mV)	-465.98	-461.46	-444.72	-449.55
I_{corr} ($\mu A/cm^2$)	**78.73**	**1.41**	**99.69**	**2.11**
β_a (mV)	82.3	52.8	68.6	56.9
β_c (mV)	98.3	132.8	98.4	142.2
Rp (ohm)	**224**	**10596**	**162**	**7409**
CR (mm/year)	**6.19**	**0.11**	**7.84**	**0.16**

Figure 2 shows friction coefficient results (COF) of Cr and GO coated ring. The average COF of Cr ring was 0.14 and the average COF of GO coated ring was 0.12. When looking the wear resistance of the Cr and GO coatings shown in Fig. 3, no wear scar was observed on GO surface while abrasive wear scars (labelled with red arrows) can be seen on the Cr surface.

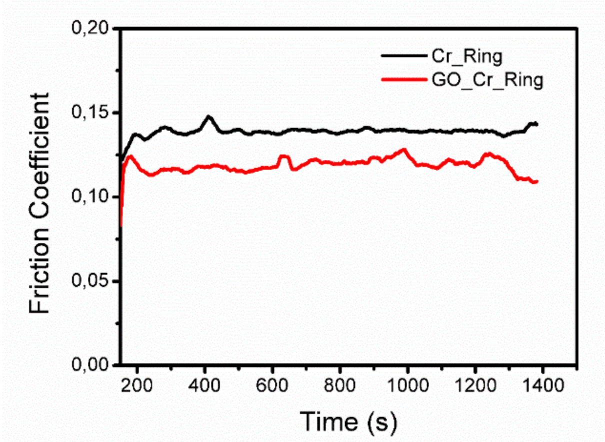

Figure 2. Friction coefficients of the Cr and GO coatings

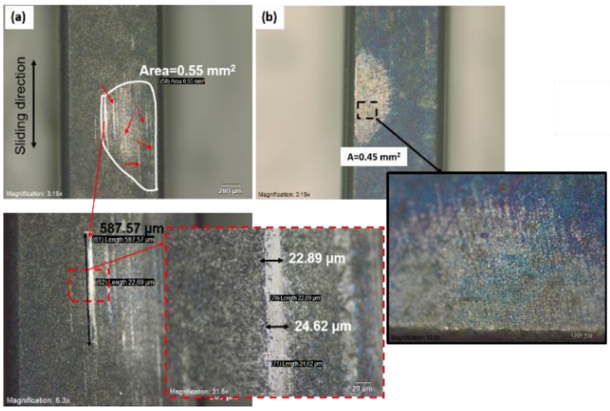

Figure 3. Optical microscopy analysis of the contact area, (a) Cr ring surface with abrasive wear scars, (b) GO coated ring with no abrasive wear scars

4. CONCLUSION

In this paper, we demonstrated a large scale directly grown GO on Cr surface via CVD method that can be a good candidate for commercial corrosion protective applications with a very low cost (only CH4, H2, and Ar gas consumption) and an excellent corrosion resistance. Furthermore, GO provided excellent wear resistance to the Cr surface, therefore, it can be a good application for piston rings of internal combustion engines.

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