Applied Surface Science 270 (2013) 526–530

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Laser surface cleaning of carbonaceous deposits on diesel engine piston

Y.C. Guan[a,*], G.K.L. Ng[a], H.Y. Zheng[a], M.H. Hong[b], X. Hong[a], Z. Zhang[c]

[a] Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore 638075, Singapore
[b] Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117576, Singapore
[c] Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore

ARTICLE INFO

Article history:
Received 27 August 2012
Received in revised form 11 January 2013
Accepted 13 January 2013
Available online 26 January 2013

Keywords:
Carbonaceous deposits
Laser cleaning
Piston
FTIR
XPS

ABSTRACT

Carbonaceous deposits of diesel engine piston are known to reduce engine durability and performance. Little research has been conducted on the deposits removal by laser technique. In this paper, the deposits on the surface of piston crown part before and after laser cleaning were examined by FTIR, XPS and SEM/EDX. The deposits were found to be distributed non-uniformly on the surface and they could be distinguished as a thicker layer of contaminants, located mainly in the plug region, while a thinner layer can be found in the remaining area. The main constituents of the deposits were analyzed as Fe_3C, Fe_3O_4, possibly FeOOH, oxygenated hydrocarbons as well as carboxylates. Laser cleaning can remove Fe_3C completely, and reduce the concentration of oxygenated hydrocarbons and carboxylates significantly. Fe_2O_3, instead of Fe_3O_4, was formed on the cleaned region.

1. Introduction

The surfaces of crowns, upper lands and ring grooves of diesel engine pistons is often covered by deposits, which is known to cause abrasive wear on the cylinder liner, leading to increased oil consumption and reduced engine durability as well as performance[1–3]. A variety of analytical work has been conducted by previous researchers on the formation of deposits and the removal of deposits [1–6]. Shurvell and Smith have reported that the composition and structure of typical diesel engine piston deposits consist of organics and inorganics compounds with thickness up to 1 μm, such as non-volatile hydrocarbon residues and partial oxidation products as well as chemically bonded layers [3,5]. It is believed that the formation of these deposits is mainly influenced by fuel composition, lubricating oil formulation, engine load, high temperature, and time [4]. The most common method to remove the deposits is using chemicals followed by scrubbing. However, this is not effective for the stubborn contaminants, especially for carbonaceous deposits [6].

As a chemically clean source with unique properties, laser offers a wide range of engineering methods to improve surface properties of materials. Among various surface processes, laser cleaning has been considered as a promising technique to directly ablate contaminants without altering or affecting bulk properties in numerous applications [7–18]. Typical applications to metallic objects are industrial settings, which includes surface preparation and coating or paint removal [7–12], biomedical implants decontamination [13,14], artwork and cultural heritage conservation and restoration [15–18]. Researchers have demonstrated that laser decontamination is able to remove micron to submicron sized surface particulates, artificially corrosion spots as well as thin contamination layer on the surface. However, little literature is available in the public domain on laser cleaning of carbonaceous deposits due to their high melting point and strong chemical bonds between the deposits and metallic substrate. Moreover, inhomogeneous carbonaceous deposits on piston surface create further challenge for laser cleaning to achieve uniform removal.

The current research was carried out to study the feasibility of laser cleaning on the inhomogeneous carbonaceous deposits from steel-based diesel engine piston. The laser used in this work was a nanosecond pulse Nd:YAG laser with a top-hat beam profiler, which is suitable for laser cleaning due to high power density and uniform energy distribution. The aim is to remove carbonaceous deposits in an effective and green way without serious degradation of essential performance to the piston substrate. Slight melting and oxidation in micron scale on the irradiated surface is acceptable because it can be potentially removed during post-treatment process. The surface chemistry before and after laser cleaning was investigated by Fourier Transform Infrared Spectrometer and X-ray Photoelectron Spectroscopy.

* Corresponding author. Tel.: +65 6793 8386; fax: +65 6791 6377.
E-mail addresses: guan0013@e.ntu.edu.sg, guanyc04@gmail.com (Y.C. Guan).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.01.075

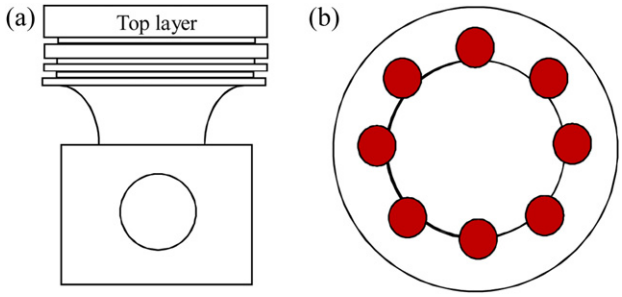

Fig. 1. Schematic diagram of one typical diesel engine piston geometry: (a) cross section for the overall profile, showing the specimen cutting from the crown of the top layer; and (b) top view for the crown, showing thick layer of contaminants as indicated in red and the thin layer of contaminants in the remaining area.

2. Experimental procedures

2.1. Sample preparation

The steel-based diesel engine piston is shown schematically in Fig. 1. The specimen were cut from the crown of a piston from the top layer, and the carbonaceous deposits were divided into two groups, one is a thick layer of contaminants as represented in red due to plug movement, and the other one is a thin layer of contaminants in the remaining area, as shown in Fig. 1 (b).

2.2. Laser cleaning

The specimens at a dimensions of 15 mm × 10 mm × 10 mm were cleaned with alcohol to reduce variation of laser beam absorption by the contaminants, and then irradiated with a pulsed Nd:YAG laser (wavelength 1064 nm) using the following parameters: average power density 1.37×10^8 W/cm^2, scanning speed 1000 mm/s, repetition rate 6 kHz, pulse duration 43 ns, and scanning 2–5 times based on thickness of deposits. The laser beam was delivered normal to the specimen surface through an optical fiber and galvanometer scanner. A focused beam was used with a square beam spot of 0.6 mm side length.

The laser-irradiated area was 10 mm × 10 mm in the hatched scanning mode with 50% overlapping. When laser was turned on, shrouding argon gas at a pressure of 1.0 bar (1.0×10^5 Pa) through a nozzle was applied to the irradiated area to minimize oxidation [19,20].

2.3. Surface analysis

2.3.1. Fourier transform infrared spectroscopy

Four areas including thick and thin layer of contaminants surfaces, laser cleaned region as well as steel substrate, were examined using a HYPERION 3000 FTIR microscope with a MCT-A detector in nitrogen environment. The contaminants and laser cleaned region were located on the cutting surface of the piston crown, as shown in Fig. 1(b). The steel substrate was located on the backside of the cutting specimen, ground with progressively finer SiC paper (180, 400, 800, 1200, 2400 and 4000 grit). All spectra were obtained in a reflection mode under a 15× IR-objective, collected using OPUS 7.0 software (Nicolet, USA) within the spectral range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}, and plotted with Microcal Origin.

2.3.2. Scanning electron microscopy/energy-dispersive X-ray spectrometry

Surface morphology was observed by Carl Zeiss EVO 50 SEM (LaB_6 filament). EDX was carried out to measure chemical composition at 5 different spots for each specimen.

2.3.3. X-ray photoelectron spectroscopy

XPS analysis was carried out for the thick layer of contaminants and laser cleaned surface using Thermo Scientific Theta Probe XPS. Monochromatic Al Ka X-ray ($h\nu$ = 1486.6 eV) was employed for analysis at an incident angle of 30° with respect to the surface normal. Photoelectrons are collected at a take-off angle of 50° with respect to the surface normal. The analyzed area is approximately 400 μm in diameter while the maximum analysis depth lies in the range of 4–10 nm. Survey spectra and high-resolution spectra were acquired for surface composition analysis and chemical state identification, respectively.

3. Results and discussion

3.1. Microscopy analysis

Fig. 2 shows a typical morphology of contaminants on the piston crown. The thin and thick contamination layers were observed on the deposits surface (Fig. 2(a)), and a closer examination of thick contamination layer reveals the rough surface covered with non-uniform deposits cluster (Fig. 2 (b)). The thickness of both thin and thick contaminants was measured as 5–20 μm by examining the cross-sectional view of the specimens, indicating much thicker contaminants than previous work [3,5,13–18].

After laser cleaning, the contaminants were largely removed, and the cleaned area became smoother compared to the deposits surface (Fig. 2(c)). It should be noted that melting effect, shown as micron scale round "particles" in Fig. 2(d), took place due to high energy density during laser cleaning. Such melting effect was unavoidable during nanosecond pulse laser irradiation due to long thermal interaction time with the material [21–24], however, such a layer can be potentially removed in the subsequent process during remanufacturing.

Quantitative analyses were summarized in Table 1. Carbon content as high as 27.9 at.% and 35.2 at.% was detected in both thin and thick contamination layers by EDX, indicating the significant presence of carbonaceous deposits. C was even higher while O was lower in thick contamination layer than those of thin contamination layer, implying that the formation of oxides was possibly suppressed by the carbonaceous growth.

After laser cleaning, Fe concentration increases nearly three to four times compared to the deposits surface, while C concentration dropped as much as 80%. Many alloying elements, such as Mn, Ca and Cr, were detected on the cleaned surface, indicating that laser cleaning is effective in removing the carbonaceous deposits. Compared to original surface without deposits, laser-cleaned surface shows a similar content of C and alloying elements, but much higher O and lower Fe concentrations, which is possibly due to insufficient prevention of oxidation during the laser processing, even though Ar assist gas is used in the process [25,26].

3.2. FTIR analysis

Typical IR spectra of original crown and laser cleaned surface are shown in Fig. 3. Data are shown as normalized absorbance over the range of 3600–800 cm^{-1}.

On the crown surface (Fig. 3(c)–(d)), the absorptions between 1700 and 1600 cm^{-1} indicate the presence of C=O carbonyl vibrations of oxidation products, while the intense IR bands between 1500 and 1380 cm^{-1} were attributed to alkyl C—H vibrations [3,5,6,27,28]. A similar absorption is assigned to oxygenated hydrocarbons and carboxylates in piston deposit analyzed by Shurvel and Diaby [5,6]. The strong absorption bands at ~1210 cm^{-1}, ~1036 cm^{-1}, and ~890 cm^{-1} in the thin layer of contaminants, are attributed to OH stretch of iron oxides including goethite