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Investigation of a self-lubricating coating for diesel engine pistons, as produced by combined microarc oxidation and electrophoresis

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ABSTRACT

The purpose of this work was to improve reliability and durability of high-silicon aluminum alloy piston skirts for diesel engines. Novel ceramic matrix composites were fabricated on ZL109 aluminum alloy substrates by two steps combining microarc oxidation (MAO) with electrophoresis deposition (EPD). MoS_2 is incorporated into an aluminum oxide matrix during processing. The effects of the ceramic matrix composites on anti-wear and selflubricating were investigated using a reciprocating test method and cylinder liner samples (boron copper cast iron) as the sliding partner. Compared to the high-silicon aluminum alloys substrate, the friction coefficient of ceramic matrix composites against the liner material was reduced by 35% under dry sliding, the wear loss was decreased by 95%, the worn surfaces were flat and smooth, and friction coefficient was relatively stable. The mechanisms by which the observed advantages were produced are discussed.

1. Introduction

In the design of diesel engines, it is important to ensure the reliability and durability of the cylinder-piston group [1,2]. The piston, which is the component of the cylinder-piston group, bears the complex thermal stress, mechanical erosion, friction and wear with the cylinder liner and so on. It is largely responsible for the life and running costs of the engine. High-silicon aluminum alloys are widely used in the piston manufacturing. However, high-silicon aluminum alloys are characteristics of low surface hardness, poor abrasion and corrosion resistance. Improving the piston reliability can decrease the malfunction rate of the engine, especially, using effective methods of surface hardening [1,2].

Composite coatings are widely applied to mechanical components due to their high mechanical, chemical and tribological properties, as well as excellent corrosion resistance [3–6]. For examples, Sun et al. prepared Ni-Al₂O₃/graphite composite coatings on LY12 aluminum alloys using a three-step process that involved electrophoresis and electrodeposition. They found that the new Ni-Al₂O₃/graphite composite coatings presented excellent lubricating properties and wear resistance due to the effects of graphite and Al₂O₃ particles [7]. Liu et al. prepared a Cu₂O–CoO/Al₂O₃ composite coating on an aluminum substrate by MAO in a phosphate electrolyte modified with Cu(Ac)₂ and Co (Ac)₂ solutions. The catalyst exhibited an excellent chemical stability with negligible leaching ions [8].

Furthermore, composite coatings containing fine particles of

graphite, SiC, Al_2O_3 , Si_3N_4 etc. can remarkably reduce the friction coefficient as well as the wear rate of the mechanical components. However, the binding modes of the substrate and composite coatings via EPD, electrodeposition, and spraying etc. include epitaxial growth, chemical bond combination, molecular bond, and mechanical bond etc., which are difficult to satisfy the requirement of pistons working conditions.

MAO is a kind of surface treatment technology including electrochemical and plasma-chemical process etc. It occurs on the surface of valve metals, such as Al, Mg, Ti, Zr, Ta, and Nb and their alloys, and forms a porous ceramic coating. The binding mode of ceramic coating and the substrate is a metallic bond combination with the highest bonding strength [9]. In our previous study, MAO has been demonstrated to significantly improve wear-resisting, and the average microhardness is more than 1200 HV. A hardness gradient exists across the coating thickness from the dense layer to the loose layer of ceramic coating [10]. However, the hardness of cylinder liner surface is far less than the dense layer, and the loose layer is easy to wear off due to the pores inside it. Although by MAO alone, we may increase the wear resistance at the surface of a piston made from high-silicon aluminum alloys, some measures must be taken to increase the wear resistance of cylinder liner surface [2], which will observably raise the costs of technology.

This work was devoted to fabricating the anti-wear and self-lubricating ceramic matrix composites on high-silicon aluminum alloys

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with MoS_2 particles in two steps by a combination of MAO and EPD, due to the good lubricating property of MoS_2 and the adaptive hardness, porous structure and excellent wear-resisting property of the MAO ceramic coating. In addition, the bonding strength of EPD coating and ceramic coating is much larger than traditional paddings, such as boiling and brush-painting methods [11]. Specifically, it can be described that the two steps are padding in micro-texture on the highsilicon aluminum alloy substrate. The padding is operated by EPD [11,12], the micro-texture is treated by MAO.

2. Experimental details

ZL109 aluminum alloy sample (wt%: 11–13% Si, 0.5–1.5% Cu, 0.8–1.3% Mg, 0.8–1.5% Ni, Residue Al. 40 mm*10 mm*10 mm) was selected to fabricate the ceramic matrix composites. The MAO electrolyte was prepared by dissolving of Na₂SiO₃, Na₂WO₃, KOH, and EDTA-2Na in deionized water. EPD electrolyte was prepared by homodisperse of acrylic anodic electrophoretic paint (10% Solid points), MoS_2 particles (10 g/l, average size: 40 nm), and polyethylene glycol (mass ratio to MoS_2 1:2) in deionized water. Meanwhile, the bath was stirred by a magnetic stirrer at a speed of 150 rpm for 30 min and then ultrasonic oscillations for 1 h by using an ultrasonic cleaner before the MAO and EPD. MAO and EPD were operated by self-developing power. First, the sample was operated by MAO for 15 min, next, cleaned by ultrasonic for 30 min. Then, the sample was operated by EPD for 1 min. Whereafter, the sample was baked for 30 min at 170 °C. Natural cooling in the end. The whole process is shown in Fig. 1.

The surface and cross-section micrographs were examined by scanning electron microscope (SEM, VEGA 3, TESCAN). The composition in ceramic matrix composites was determined by X-ray diffraction (XRD, EMPYREAN) and energy dispersive x-ray spectroscopy (EDXS) coupled to the SEM. The wear resistance of the ceramic matrix composites was tested under dry sliding conditions in the atmosphere at room temperature by the reciprocating friction and wear tester (selfdeveloping, DALIAN MARITIME UNIVERSITY).

3. Results and discussion

3.1. composition and morphology

Surface morphologies of the ceramic coating and the ceramic matrix composites are shown in Fig. 2.

The SEM micrograph of the ceramic coating surface, as illustrated in Fig. 2A, shows that the ceramic coating surface is characteristic of a porous structure of ups and downs, with a thickness of approximately 10 μ m (Fig. 1B). The surface structure of ceramic coating is the important basic condition of EPD and self-lubricating ceramic matrix composites, because EPD requires having an electric field, meanwhile the regions of pores and thinner coatings provide stronger electric field intensity. So EPD prefers forming in the regions of pores and thinner

coatings, then forms a uniform coating on the ceramic coating, with a thickness of approximately 10 μ m (Fig. 1C). The morphology of ups and downs also improves the bonding strength between ceramic coating and EPD coating by inlaying. As is illustrated in Fig. S1A, B, the white flake materials are MoS₂. So the regions of pores and thinner coatings contain much more MoS₂ wrapped by electrophoretic paint (Fig. 2B, C and Fig. 1C). In the process of friction and wear, although the EPD coating may be worn, the ceramic coating has much better wear-resisting property. MoS₂ retained in the regions of pores and thinner coatings, would continue to play a role of anti-wear and self-lubricating. Therefore, the preparation of ceramic matrix composites requires the porous structure and appropriate thickness of the ceramic coating. The larger ceramic coating thickness is, the greater power is required.

Fig. 3A shows the XRD spectra of the ceramic coating and the ceramic matrix composites. Because of the porous structure, there are remarkable Al and γ -Al₂O₃ peaks for the ceramic coating (Fig. 3A (a)). It is seen that there are not only typical Al and γ -Al₂O₃ peaks for the ceramic matrix composites, but also the (002) where 2 θ is 14.331° (Fig. 3A (b)) when compared with the XRD spectrum of the ceramic coating. This observation demonstrates incorporation of MoS₂ particles into the ceramic matrix composites. This result further indicates that the combination method belongs to a mechanical combination.

3.2. Friction and wear properties

In the present research, the anti-friction and wear resistance of the ceramic matrix composites were examined by the reciprocating friction and wear tester driven by a servo motor. The sliding counterbody material is boron copper cast iron which is used as a predominant material of cylinder liner in diesel engine design for the higher hardness and wear resistance. The friction pairs were the ZL109 aluminum alloy (40 mm*10 mm*10 mm) and cylinder liner samples (boron copper cast iron, 110 mm*10 mm*2 mm), the ceramic matrix composites (40 mm*10 mm*10 mm) and cylinder liner samples (110 mm*10 mm*2 mm). The test was carried out with 20 N loading at 0.2 m/s sliding speed for 5 min. Each sample was cleaned by ultrasonic washing in absolute ethyl alcohol before and after the test, so as to reduce the impurities on the surface of samples which may affect the whole wear test, and thus to improve the calculation accuracy of the weight loss and reduce the fluctuation of the friction coefficients. The friction coefficient and sliding time were obtained automatically during the test by acquisition cards, transducers and software for collecting information. The weight loss of samples was measured by weighing the samples before and after each wear test, using an electrical balance with a precision of 0.1 mg. Five samples of each set of conditions were tested for each data, so as to avoid the fluctuations in the data, and the reported values are the average resulted from these measurements.

The purpose of the test is to prove the self-lubrication property of the ceramic matrix composites itself. If the tests had run with



Fig. 1. Scheme showing the two-step method of ceramic matrix composites: (A) cross-section morphology of ZL109 aluminum alloy substrate. (B) cross-section morphology of the ZL109 aluminum alloy substrate after MAO. (C) cross-section morphology of the ZL109 aluminum alloy substrate after MAO and EPD. 1. ZL109 aluminum alloy substrate. 2. MAO ceramic coating. 3. EPD coating. 4. MAO for 15 min 5. EPD for 1 min.

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