Electroless Ni-P-C\(_g\) (graphite)-SiC composite coating and its application onto piston rings of a small two stroke utility engine

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Received 18 June 2010; revised 18 August 2010; accepted 19 August 2010

This study presents electroless Ni-P-C\(_g\) (graphite)-SiC composite coating deposition onto piston rings of a small two stroke utility engine at 90°C under C\(_g\) (10 g/l) and SiC (8 g/l) concentration at agitation speeds of 160 rpm. Coating showed compact embedding of C\(_g\) and SiC particles in Ni matrix, uniformly and largely distributed in coating by mechanical stirring. Heat-treatment of coating increased microhardness due to crystallization of a hard Ni\(_3\)P phase after heat treatment. An average surface roughness of a standard piston ring has improved from 1.095 \(\mu\)m to 0.900 \(\mu\)m, with a lower friction coefficient of coated (0.18) as compared to uncoated (0.23) surface.

Keywords: Composite coating, Electroless plating, Ni-P-C\(_g\)(Graphite)-SiC coating

Introduction

Metal matrix composites containing ceramic particles as a distributed phase are useful in engineering\(^1\). Among various methods to prepare particle-dispersed metal matrix composites\(^2\), most common method is composite plating. Incorporation of particles into a metal matrix by composite plating is based on electro-\(^3\) and electroless\(^4\) plating techniques. For preparing dispersion-hardened alloys, electroless deposition is an economic and suitable method of producing composite coatings (CCs). Electroless deposition of nano-sized particles is more difficult than that of macro-sized particles and also due to agglomeration of nano-sized particles in plating bath\(^5\). Mechanical and tribological properties of Ni coating get improved by incorporation of different solid particles\(^6\). Huang et al\(^7\) discussed microstructure and properties of Ni-P-PTFE-SiC. Losiewicz et al\(^8\) reported phase composition and surface morphology of electrolytic Ni-P-TiO\(_2\)-PTFE composites for an electrochemical reaction electrode. Deng et al\(^9\) discussed electrodeposited Re-Ni-W-SiC-PTFE composite and their properties.

In order to improve physical and mechanical properties of coatings, CCs based on nickel (Ni/SiC\(^10\), Ni/ZrO\(_2\)^{11}, Ni/Al\(_2\)O\(_3\)^{12}, Ni/WC\(^{13}\) and Ni/B\(^{14}\)) have been developed by electrodeposition method. In these materials, Ni deposits provide anti-corrosion properties and incorporation of hard and lubricating particles (SiC and C\(_g\)) provide mechanical and tribological performances. Electroless Ni-P coating has a high plating capability, high bonding strength, excellent weldability and good antiwear. C\(_g\) can keep constant friction coefficient under high temperature and high sliding velocity because it is insensitive to temperature\(^15\). SiC particle has properties such as low price, good chemical stability, high microhardness and wear resistance at high-temperatures. Tribological behavior of electroless Ni-P-Gr-SiC composite\(^16\) and electroless Ni-P-C\(_g\)(graphite)-SiC composite coating\(^17\) has already been studied.

This study presents electroless Ni-P-C\(_g\)-SiC CCs on a piston ring’s substrate of a small two stroke utility engine.

Experimental Section

Materials

A typical nickel bath plating solution was prepared for electroless deposition, then SiC (10 g/l; size, 10 \(\mu\)m) and C\(_g\) (8 g/l; size, 20 \(\mu\)m) particles were added. Bath consists of nickel sulfate (NiSO\(_4\).6H\(_2\)O, Merck; 30 g/l), sodium hypophosphite (NaH\(_2\)PO\(_2\).H\(_2\)O, Merck; 25 g/l), sodium citrate (C\(_6\)H\(_5\)Na\(_3\)O\(_7\).2H\(_2\)O, Merck; 20 g/l), glycine
(C₃H₅NO₂, Fluka; 20 g/l), and lead nitrate (2 g/l). These analytical reagent grade chemicals were added to deionize water to form an electroless bath solution. Trace hexadecylpiridinium bromide (0.3 g/l) as a brightener and dodecyl sodium sulfate (0.1 g/l) as a surfactant were added for a more uniform Ni deposition. Experiments were performed at pH 4.6 - 4.9 and temperature 90°C. Cast iron of actual piston rings was used as substrate. All sides of piston rings substrate were plated (area of deposition, 7.5 cm²). All piston rings were rinsed in NaOH (10%) solution for 5 min to remove surface contaminants, cleaned ultrasonically (JAC Ultrasonic1002), and finally put into bath plating solution for co-deposition.

Methods

For co-deposition process, which was carried out for 150 min to form 47 μm thick product, mechanical stirrer (Heidolph RZR 2041) method was applied at 160 rpm. When electroless plating was completed, piston rings were taken out of solution and rinsed in water. Then coated piston rings were fixed with epoxy resin for metallurgical analysis. Preliminary microstructure analysis of coating was studied under light optical microscopy (Olympus BX51M). Zeiss SUPRA™ 35VP FESEM/EDS was used for microstructure and elemental analysis. An FV-7 Vickers hardness tester (load, 0.5 kgf; indentation time, 8 s) was used for hardness measurements of CCs. Average surface roughness of standard piston rings and CC were analyzed using an Alicona Infinite Focus 3-D optical microscope. Crystallization of CCs was analyzed using Bruker D8 Advance X-Ray Diffractometer.

Tribological properties of standard piston rings and CC (Ni-P-Cg-SiC) piston rings were measured by friction test at various speeds. Piston assembly of frictional force measurement is a two stroke single cylinder small engine. It consists of two similar compression rings. Friction force measurement of piston assembly was carried out using 4-components Kistler Type 9272 load cell, which was connected to multi channel amplifier and friction force was plotted against time by Integrated Measurement & Control software in computer. Piston assembly was mounted on the top of load cell. Friction force of piston and cylinder wall acted in Y direction of load cell. Piston assembly does not allow firing and is powered by AC motor. Speed of rotation was controlled by speed controller device (Emerson, Commander SK).

Results and Discussion

CC of Ni-P-Cg-SiC was successfully co-deposited on all sample surfaces with an acceptable homogeneity. Cg and SiC particles, a neutral constituent, retained their chemical stability throughout the process. However, as Cg and SiC particles were introduced into electroless bath solution, stirring for particle suspension were tailored without any interference in Ni²⁺ ion for Ni electroless deposition. Therefore, a Ni matrix was able to be deposited using suitable stirring procedures. Cg and SiC particles were also efficiently co-deposited.

From FESEM image of cross-section of Ni-P-Cg-SiC CC on piston ring substrate and actual uncoated piston ring (Fig. 1), coated layer was found brighter compared to uncoated one. Fig. 2 shows cross sectional area of CC under FESEM analysis. Black stripes and dots at
Ni-P-Cg-SiC layer represent Cg and SiC particles, respectively. Agitation rate (160 rpm) was able to force Cg and SiC particles to be co-deposited. In addition, an agglomeration of Cg and SiC particles was not present. FESEM result showed that bonding of Ni, P, SiC and Cg is compact.

Increase in hardness resulted after Ni-P-Cg-SiC CC due to existence of SiC particles. It further increased after heat-treatment (Fig. 3) at 400°C for 1 h, due to crystallization of a hard Ni₃P phase (ICDD 00-034-0501). Average microhardness of standard piston rings surface improved significantly after Ni-P-Cg-SiC CC. It further
increased after heat-treatment of this CC at 400°C for 1 h from 283 Hv to 851 Hv (Fig. 4). Imprint of indentations obtained for uncoated piston ring was larger than imprint obtained for Ni-P-Cg-SiC CC piston ring (Fig. 5). Hardness measured for uncoated piston rings substrate was 283 Hv as compared to 406 Hv for Ni-P-Cg-SiC CC piston rings and 851 Hv after heat treatment. Therefore, effects of SiC particles and crystallization of a hard Ni$_3$P phase after heat treatment influenced in increasing coating hardness.

Surface roughness (Ra) is arithmetic mean of absolute values of distances from mean line of valleys and peaks. Rt is distance between highest peak and deepest valley. Rz is arithmetic mean of differences between 5 highest peaks and 5 lowest valleys. All values refer to length of measurement. Average Ra of uncoated piston rings and electroless Ni-P-Cg-SiC CC in as-deposited and annealed state improved from 1.095 µm to 0.900 µm (Fig. 6).

Introduction of C$_g$ particles into Ni-P coating effectively reduced friction coefficient, due to loose surface of coatings co-deposited with C$_g$ particles. Graphite can keep constant friction coefficient under high temperature and high sliding velocity due to its temperature insensitivity. Ni-P-Cg-SiC CC piston rings (Fig. 7) had lower friction coefficient (0.18) as compared to uncoated piston rings (0.23), due to formation of C$_g$ film between coating and counterpart during sliding. It was attributed to lower Ra of Ni-P-Cg-SiC CC piston rings (0.900 µm) as compared to 1.095 µm in uncoated piston rings. CC (Ni-P-Cg-SiC) with high hardness, low friction coefficient and lower Ra is beneficial for counterpart action along revolution direction.
Conclusions

Ni-P-Cg-SiC CC was successfully co-deposited on actual piston rings of a small two stroke utility engine. Cg and SiC particles compactly embedded into Ni matrix. Average surface roughness of standard piston rings improved from 1.095 $\mu$m to 0.900 $\mu$m, with a lower friction coefficient of coated (0.18) than uncoated (0.23) surface. Average microhardness of standard piston rings surface significantly improved after Ni-P-Cg-SiC CC and further increased after heat-treatment of this CC at 400°C for 1 h from 283 to 851 Hv.

Acknowledgements

Authors thank Universiti Sains Malaysia for support, and also thank Mr Abdul Rashid Selamat & Mr Mohd Asshamudin Hashim for technical assistance.

References