Surface & Coatings Technology 315 (2017) 490–497

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Effects of phosphate binder on the lubricity and wear resistance of graphite coating at elevated temperatures

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ARTICLE INFO

Article history:
Received 21 December 2016
Revised 1 March 2017
Accepted in revised form 5 March 2017
Available online 06 March 2017

Keywords:
Phosphate binder
Graphite
High temperature lubricity
Tribological properties

ABSTRACT

To achieve a kind of graphite-based bonded solid lubricating coating with excellent lubricity at high temperature, a graphite coating was fabricated on Inconel 718 substrate using a binder of aluminum chromium phosphate (ACP). The sliding friction and wear behavior of the coatings was evaluated by a reciprocating alumina ball-on-flat specimen geometry from room temperature (RT) to 700 °C. The structures and morphologies of the graphite phosphate coating were analyzed by X-ray diffraction, Fourier transform infrared spectrometry, X-ray photoelectron spectroscopy, Raman spectroscopy and scanning electron microscopy. The graphite phosphate coating exhibited stable and low friction coefficients from RT to 700 °C, except for the range of 200–300 °C. Results are explained on the basis of a reaction between phosphorus in the ACP binder and the dangling covalent bonds of the graphite to prevent its oxidation. Simultaneously, the elimination of adsorbed water vapor and the presence of a large degree of crystal defects in the graphite are responsible for the failure of the graphite phosphate coating at 200–300 °C. As a result, the wear mechanism of graphite phosphate coating at elevated temperatures is particularly analyzed and discussed in this work.

1. Introduction

As one of the most practical and maturest coating technologies, bonded solid lubricating coatings, also known as dry lubricating film, are widely used in the fields of aeronautics and astronautics, weaponry, manufacturing, and so on, due to their outstanding friction-reducing and anti-wear properties [1–5]. It is common knowledge that the indispensable component is binder, which contains organic resin binders and inorganic binders. Generally speaking, epoxy, phenolic, polyimide and acrylic resins are traditional organic resin binders, phosphate and silicate are the most common inorganic binders [6]. Inorganic binders are of extraordinary significance for improving the thermal stability and high-temperature resistance of bonded solid lubricating coating; and in particular, phosphate binder has particular advantages, due to its strong adhesion, good impact resistance, low coefficient of thermal expansion, excellent dielectric behavior, low curing temperature and good high-temperature resistance [7–9]. We have found in our previous reports that phosphate binder exhibits satisfactory high-temperature performance for bonded solid lubricating coatings which were used to solve the problem of friction and abrasion [10,11].

As one of the most commonly used solid lubricants, the scientific reports of graphite lubrication are extremely extensive [12–14]. Nevertheless, as a conventional solid lubricant, the application of graphite is restricted by the inferior oxidation resistance at much lower temperature. Depending on the nature of graphite, oxidation may commence at temperatures as low as 400 °C in the presence of oxygen [15,16], leading to subsequent gasification to CO_2, which in turn, leads to a significant degradation in the structural properties of the material [17]. To overcome this drawback, some researchers have established various oxidation protection methods of carbon materials including carbon fibers, carbon-carbon composites and graphite [18–20]. For example, chemical vapor deposition (CVD) of ceramic coatings [21,22] and surface treatment with aqueous solutions containing boron or phosphorus [23,24] have been found to be of significance for the oxidation protection of carbon materials. Compared with the two common oxidation protection methods of carbon materials, the solution technique is more effortless and economical than the CVD method. More importantly, numbers of researchers took advantage of aluminum phosphate to treat with carbon fiber and graphite, which could increase the onset oxidation temperature by approximately 75–100 °C [17,25].

Inspired by the abovementioned perspectives, the most important issue in lubricity of graphite at elevated temperature is the necessity to render graphite resistant to oxidation. Thus, it occurs to us that, if we combine phosphate binder with graphite, the oxidation resistance of graphite would be enhanced at elevated temperatures. Then we will be able to obtain a good chance to acquire graphite-based bonded solid lubricating coatings with greatly improved thermal stability.

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http://dx.doi.org/10.1016/j.surfcoat.2017.03.013
0257-8972/

Herein we select aluminum chromium phosphate with excellent high-temperature chemical stability, thermal insulation and oxidation resistance (it can withstand temperature as high as 1200 °C) [7,26] as the adhesive system to prepare graphite bonded solid lubricating coating. Such a potential combination will develop graphite-based solid lubricating coatings that can work at higher temperatures, even in a wide-temperature range. The innovation point of the work is to exploit the traditional solid lubricant of graphite to break through its restriction in nature and broaden the prospect of applications in the field of tribology.

2. Experiments

2.1. Preparation of aluminum chromium phosphate binder

Aluminum chromium phosphate binder (ACP) was prepared with orthophosphoric acid (H_3PO_4, 97 wt%), aluminum hydroxide ($Al(OH)_3$, 97 wt%) and chromium oxide (CrO_3, 99 wt%) by a mole ratio of $n(H_3PO_4)$: $n(Al(OH)_3)$: $n(CrO_3)$ = 12: 3: 1. Briefly, H_3PO_4 was placed in a three-necked-bottomed flask and diluted to 65 wt% with deionized water, and then CrO_3 was dissolved in the acidic solution. The resultant mixed solution was heated to 80 °C, followed by the addition of $Al(OH)_3$ when the mixed solution became optically clear. The reactant mixture was further heated up to 110 °C and kept the reaction at this temperature for 3 h to achieve aluminum chromium phosphate binder for preparing bonded solid lubricating coatings.

2.2. Preparation of phosphate lubricating coatings

Commercially available lubricating filler flake graphite was blended with ACP binder at a fixed mass ratio of 1:1.5. Subsequently, the slurry was mixed by mechanical stirring and ultrasonic vibration to achieve even dispersion of the solid lubricant filler in the mixed paint, where the diameter size of flake was 3–5 μm. Before the preparation of coatings, the Inconel 718 substrate surfaces were cleaned and roughened to a surface roughness (*Ra*) of 2.00 ± 0.20 μm by sandblasting with SiO_2 grit of 50–100 μm, and ultrasonically cleaned with acetone for 15 min in order to improve the adhesion of the phosphate coatings to the substrate. Then the mixed paint was sprayed onto the disc (24 mm in diameter and 7.8 mm in thickness) using a spray gun with 0.2 MPa N_2 gas. After solvent evaporation, the coating specimens were cured at 120 °C for 2 h and 310 °C for 1 h in a muffle furnace to achieve as-fabricated phosphate coatings with a thickness of 15–20 μm (measured with MINITEST 1100 microprocessor coating thickness gauge).

2.3. Friction and wear tests

The friction and wear behavior of the phosphate coating was evaluated with an Optimol SRV-IV oscillating friction and wear tester in a ball-on-flat contact configuration. The counterpart available Al_2O_3 ball (diameter 9.8 mm; hardness 1650 HV) was driven to slide against the coatings on Inconel 718 disc at a reciprocating distance of 1 mm, an oscillatory frequency of 5 Hz, a normal load of 10 N, a sliding duration of 20 min, and temperatures of room temperature (about 25 °C), 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. The friction coefficients were automatically measured and recorded by the computer connected to the test rig, and the temperature was measured in the wear tests by a thermocouple connected to the sample pedestal and recorded by the computer. A MicroXAM 3D non-contact surface mapping profiler was used to measure the wear volume loss (ΔV, unit: mm^3) of the worn surfaces. The wear rate (unit: $mm^3/(N\cdot m)$) is calculated as $Ws = \Delta V/SF$, where S refers to the total sliding distance in m and F is the applied load in N. Three coated specimens were used in the friction and wear tests at each temperature under the same condition, which was to obtain reliable data with minimized scattering. The average values of the data of three repeat tests are cited in this article.

2.4. Characterization techniques

A Philips X'Pert-MRD X-ray diffractometer (XRD) was used to identify the phase composition of the coatings (40 kV, 30 mA, Cu-Kα radiation; scanning within 2θ = 10–80°). A Netzsch STA-409 PG/PC Jupiter Analyst was employed to evaluate thermogravimetric-differential scanning calorimetric (TG-DSC) analysis of the pure graphite filler and the mixture of graphite with ACP binder (heating rate: 10 °C/min) from RT to 1000 °C under air environment. The morphologies of surface and worn surface of the coatings were observed using a JSM-5600LV scanning electron microscope (SEM; acceleration voltage: 20 kV) equipped with an energy dispersive X-ray spectrometer (EDX). The local chemical structure of the tested samples were identified with a Nicolet NEXUS FTIR spectrometer in the wave number range of 4000–400 cm^{-1}, a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS) (monochromated AL Kα radiation; pass energy 29.4 eV), in which the binding energy of carbon contaminant (C1s: 284.8 eV) was adopted as the reference, and a LabRAM HR800 micro-Raman spectrometer operating with a 532 nm Ar^+ laser as the excitation source.

3. Results and discussion

3.1. Characterization of the graphite bonded solid lubricating coating

Fig. 1 displays the XRD patterns of the Inconel 718, graphite phosphate coating after curing and graphite phosphate coating after treating at 700 °C. It can be seen that only graphite is identified in the cured coating, no diffraction peaks of Udimet alloy ($Ni_3(Al,Ti)$), taenite (Fe,Ni) phases which are the main components of Inconel 718. Besides, no peaks of aluminum chromium phosphate are detected in the XRD patterns, which due to aluminum chromium phosphate is amorphous below 600 °C [10]. After treating in a muffle furnace at 700 °C, graphite and Al_2O_3 are identified in the graphite phosphate coating. No Cr_2O_3 can be found because its content is too low to be detected.

The SEM morphologies and elemental distributions of Inconel 718 substrate and as-fabricated graphite phosphate coating are shown in Fig. 2. The sample preparation technique of the coating cross section as shown in Fig. 2a is used a line cutting machine. The cutting begins at the Inconel 718 substrate, the reverse side of the coating, and stops when the molybdenum wire (the cutting material of the cutting machine) reaching the underneath of the interface between coating and substrate. The displacement distance has been measured based on the thickness of substrate and set in the parameter before the cutting. The immediately fractured sample is broke off through mechanical force. At last, the fractured sample is inlaid in epoxy resin and polished after curing of the resin. The as-prepared coating cross section is ready for

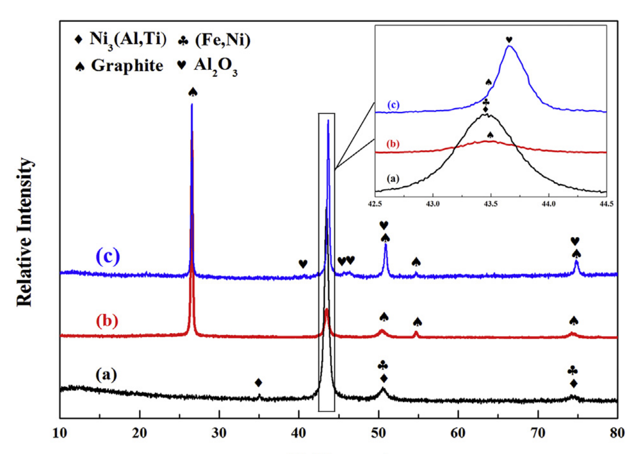

Fig. 1. XRD patterns of Inconel 718 substrate, graphite phosphate coating after curing and treating at 700 °C.