Diamond-like carbon coatings fabricated by the ball impact process

Naohito Hayashi *, Tatsuya Oki

Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Japan

HIGHLIGHTS

- Mechanochemical fabrication of DLC coatings by the ball impact process.
- DLC structure in the fabricated coatings disappears with extended treatment time.
- The threshold of maximum vibration acceleration of the chamber is 39 m/s^2.
- The threshold of contact stress acting on the substrate surface is 1500–2000 MPa.

ARTICLE INFO

ABSTRACT

Favorable physical properties of diamond-like carbon (DLC) coatings such as high hardness, low friction, and high wear resistance are responsible for their widespread use in many industrial applications. However, suboptimal high-energy and high-cost processes, e.g., plasma CVD, are currently utilized in the industry for coating DLC. In this study, the ball impact process—a method for low-energy and low-cost metal surface treatment—was employed for coating DLC directly. The process involves the initiation of a mechanochemical reaction on a substrate surface in a methane gas atmosphere over several minutes. Repeated ball collisions are expected to generate coatings cores at the crystal grain boundaries of the substrate surface, followed by subsequent growth into interference color coatings with a DLC structure. Additional ball collisions destruct the interference color coatings and cause pyrolysis by a mechanochemical reaction, which are subsequently transformed to black carbon coatings without DLC structures. Because these changes proceed with extended treatment times, an optimum treatment time to obtain an ideal substrate surface coating exists. Based on the comparison between the experimental results obtained by varying the vibration frequency and the results of numerical simulations of ball behaviors using the discrete element method, the frequency threshold for fabricating DLC coatings was found to be 5 Hz (maximum vibration acceleration: 39 m/s^2). This corresponds to a contact stress in the range 1500–2000 MPa acting on the substrate surface.

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1. Introduction

Diamond-like carbon (DLC)—a form of amorphous carbon composed of carbon atoms with both sp3 and sp2 bonds that are found in diamond and graphite structures, respectively—was first synthesized by Aisenberg and Chabot [1] by an ion beam deposition method. Generally, DLC contains a certain percentage of hydrogen [2,3]; a 1-μm-thick DLC-coated surface has a small friction coefficient of approximately 0.1 and roughness of approximately 0.1 μm, with a Vickers hardness of approximately 3000 HV [4–7]. In addition, DLC coatings show high biocompatibility [8–11]. Because of these excellent properties, a wide range of applications involving DLC coatings have been developed for use across industries. In particular, investigations into fuel consumption optimiza-

tion by deployment of DLC coatings have generated much interest from the automobile industry, because the low friction properties of DLC coatings contribute greatly to decrease friction losses at sliding surfaces in car engines [3,12–16].

Two common methods for coating DLC are currently in use: first, physical vapor deposition (PVD) method, which involves the fabrication of DLC coatings from a solid carbon source using sputtering [5,17–19], ion beam deposition [1,20,21], and laser beam abrasion [22–27] under high vacuum; and second, chemical vapor deposition (CVD) method, in which hydrocarbon gases such as acetylene or methane are ionized by a plasma discharge. The generated hydrocarbon ions are then forced to accelerate and undergo collision to form coatings on a negatively-charged substrate [2,25,28–32]. Recently, a process for synthesizing DLC coatings at sub-ambient or ambient pressures has been developed [33,34]. However, both these methods require high energy and expensive machinery for coating DLC. Therefore, new DLC coating methods

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* Corresponding author. Tel.: +81 29 849 1110; fax: +81 29 861 8472.
  E-mail address: n.hayashi@aist.go.jp (N. Hayashi).

with significant reductions in energy as well as cost are required to enable their widespread use.

In the present study, the synthesis of DLC materials by mechanochemical reactions and the fabrication of DLC coatings were attempted by employing the ball impact process. This technique involves a novel dry-surface treatment of metals, previously developed by the authors of the present paper [35], in which metal or ceramic balls and powder particles are placed inside a vibration chamber, which is mechanically vibrated. This action causes the balls to accelerate and repeatedly impact the inner metal surface of the chamber. As a result, the metal surface is rapidly coated with the powder particles. During the ball impact process (Fig. 1), the particles are abraded and sandwiched between the balls and the inner wall of the chamber, which binds the particles to each other by a cold welding process, thereby forming a particle coating. High-density adhesive particle coatings can be fabricated through this process under ambient temperature, normal pressure, and in a standard air atmosphere. Using mechanical vibrations, the authors have successfully fabricated a high-temperature corrosion-preventive coating of $LaPO_4$ particles on a stainless steel (SUS) substrate [36,37], a coating of TiN nanoparticles on a metal substrate to improve surface hardness [38], and a coating of hydroxyapatite (HAp) particles on a Ti substrate to fabricate a biocompatible material with good mechanical strength and osteoconductivity [39].

The main purpose of this paper is to demonstrate a novel, low-energy, and low-cost process principal for the fabrication of DLC coatings on metal substrates within several minutes. The ball impact process was applied without powder particles, in a methane-gas atmosphere at ambient temperature. The effects of changes in treatment time and vibration frequency were investigated. Properties of the fabricated coatings were examined by optical microscopy observations and Raman spectroscopic analysis. In addition, numerical simulations of ball behavior based on the discrete element method (DEM) were conducted to investigate the relationship between the contact stress acting on the substrate and the probability for the fabrication of DLC coatings.

2. Experimental

2.1. Apparatus and method

The apparatus for the ball impact process was the same as that for the fabrication of HAp particle coatings on Ti substrates [39]. In our previous paper [14] on the system design of the ball impact process, some discussion of cases in which the substrate to be coated was large or complicated in shape, rather than being plate, was included. In order to substitute air with methane gas, an atmosphere control box covered the vibration chamber. A ZrO_2 mill pot (volume: 45 mL; diameter: 40 mm; height: 40 mm) was used as the chamber. A prescribed number of balls were placed into the
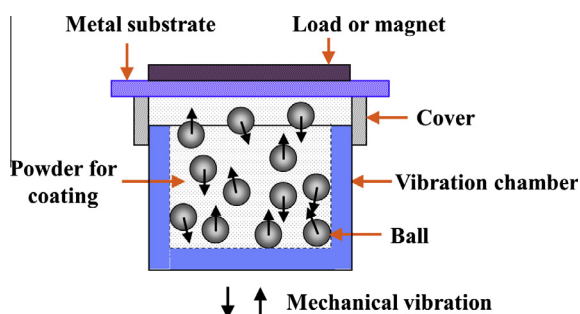

Fig. 1. Process concept of the ball impact process.

chamber and the chamber was covered with a SUS substrate. Before the start of the experiment, vacuuming of the control box and methane gas injection were repeated three times to prepare a suitable methane gas atmosphere of 1 atm. In situations where the substrate size is bigger than the box, or its surface shape is so complex as to prevent the sealing cover from working properly, additional machinery is required including continuous hydrocarbon gas injection to the coating surface, and recovery and recycle of the used gas.

The experiments commenced as soon as the vibration frequency reached the prescribed value (within seconds).

2.2. Materials

Methane gas of 99.99% purity was used in the experiments. Pure SUS304 plates (after acid pickling; length and breadth: 50 mm; thickness: 2 mm) were prepared as the substrates to be coated. The reason for using a SUS304 substrate was consideration of future practical use, specifically looking at increasing the wear resistance of sliding surfaces in car engines and brakes made of steel. In addition, the fact that SUS is a typical metal material also played a part, as the ball impact process has a lot of flexibility when it comes to choosing substrate materials and atmosphere gases. Prior to the experiments, the plates were first washed with ethanol and subsequently with distilled water in an ultrasonic bath. The vibration chamber and balls were made of ZrO_2, and the ball diameter was 5 mm.

2.3. Conditions

It is possible to set the amplitude and frequency of the vibration chamber independently and arbitrarily. However, because the mechanical load due to the sinusoidal excitation force increases dramatically when a higher amplitude and frequency are employed, the amplitude used was fixed at 40 mm and the frequency was limited to 20 Hz, these conditions are similar to those used in a previous research [39].

First, experiments were conducted with a ball-filling fraction of 11% (mass: 50 g; number: 75) within the vibration chamber and 1–20 min of treatment time. Next, the treatment time was fixed at 10 min and the vibration frequency was varied from 3 to 20 Hz.

2.4. Analytical methods

After the experiments, optical microscope observations and Raman spectroscopic analyses (Thermo Scientific, DXR Raman Microscope) were conducted. For the Raman spectroscopic analysis, a laser light of wavelength 532 nm was used; its measurement range was approximately 1 μm along the radial direction and 2 μm along the depth direction. From the spectra obtained, the peaks found near the D band (around 1330 cm^{-1}; indicating the existence of sp3 carbon bonds) and the G band (around 1580 cm^{-1}; indicating the existence of sp2 bonds) were identified and separated by using the Gauss-Lorentz function. The ratio of the D-band peak intensity to the G-band peak intensity (I_D/I_G) was then calculated for each spectrum.

3. Numerical simulation

3.1. Simulation model

DEM [40] is a well-known method for simulating powder behavior, in which the behavior of the particles that constitute the powder is calculated using motion equations derived by considering all forces acting on the particles. In the DEM, the effects of contact among the particles in normal and tangential directions