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# Corrosion performance of DLC coatings with laser-induced graphitized periodic surface structure



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#### ABSTRACT

Two types of diamond-like carbon (DLC) thin films, hydrogenated amorphous carbon (a-C:H) and super-hard tetrahedral amorphous carbon (ta-C), were irradiated with femtosecond laser pulses, and the corrosion resistance of the DLC films with laser-induced periodic surface structure (LIPSS) and modified to nanocrystalline graphite (nc-G) was electrochemically evaluated from anodic polarization measurements. The polarization curve for a glassy carbon (GC) plate, which is a type of nc-G, was measured for comparison. The polarization curve for stainless steel with LIPSS was also measured, and it was confirmed that LIPSS increased the surface area of the irradiated part, which resulted in an increased apparent corrosion current density. Polarization curve measurements for irradiated DLC indicated that the corrosion current density was reduced, despite the effect of an increased surface area by the formation of LIPSS, and the polarization curves tended to approach those for GC plates. Therefore, the irradiated surface layer of DLC is modified to nc-G, which results in excellent corrosion resistance similar to that of GC.

### 1. Introduction

Diamond-like carbon (DLC) thin films are smooth, have high hardness, low adhesion and low friction, and exhibit excellent chemical inertness and biocompatibility, so that DLC films have recently been used in many industrial products and biomedical applications [1-4]. DLC is classified into four types according to high or low  $sp^3$  content and whether or not hydrogen is included. DLC that does not contain hydrogen is classified as tetrahedral amorphous carbon with a high  $sp^3$ content (ta-C) and amorphous carbon with a low  $sp^3$  content (a-C), while DLC types that contain hydrogen are classified into hydrogenated ta-C (ta-C:H) and hydrogenated a-C (a-C:H). Among these types, the a-C:H films are applied in industry, and examples of their applications are expanding. On the other hand, hydrogen-free ta-C films with properties close to those of diamond have ultra-high hardness, high density, and excellent wear and heat resistance, and have recently been employed in tribology-related applications, such as in automotive parts, and their applications have expanded and thus attracted more attention [5,6]. DLC coatings are also expected to provide protection for substrates, and the effect of Si addition [7] and the corrosion resistance of DLC coatings in various aqueous solutions (NaCl, HCl, H<sub>2</sub>SO<sub>4</sub>) [8-11] using electrochemical evaluation methods has been reported. Furthermore, to improve corrosion resistance, the effects of interlayer insertion [12], ion implantation [13], and the addition of other elements [14] into DLC films have been reported. The effect of multi-layering of ta-C ultra-thin films with a different  $sp^3$  ratio [15] has also been reported recently. There are also increasing reports of tribocorrosion with DLC using wear tests in liquids, which is a more stringent assessment method [16,17].

Femtosecond (fs) lasers are capable of precision micromachining with extremely low thermal effects on difficult-to-process materials such as DLC, and fine laser-induced periodic surface structure (LIPSS) can be easily formed on DLC surfaces [18–21]. The origin of nanoscale periodicity in fs-LIPSS can be attributed to the excitation of surface plasmon polaritons, which induce the periodic enhancement of local fields in the surface layer [18,19]. The  $sp^3$  sites in DLC films are also converted to  $sp^2$  sites by fs-laser irradiation, so that DLC is modified to nanocrystalline graphite (nc-G) accompanied by an expansion in volume [22–26]. Fs-LIPSS has been increasingly reported as a surface modification method to optimize the frictional, wetting, optical, biological, and reactivity properties of a specimen surface [21]. Graphitization and swelling occur at the same time in DLC; therefore, it is expected to lead to new surface modification technologies. There has also

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