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Protecting carbon steel from corrosion by laser *in situ* grown graphene films

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ABSTRACT

Corrosion of metals causes tremendous financial loss and disasters every year. Graphene is a promising candidate for anti-corrosion coating, due to its unique properties, *e.g.* chemical inertness, impermeability and high conductivity. Despite being a commercially important material, it is difficult to grow graphene on carbon steels and is therefore prominently grown on copper or nickel substrates. Here, we report a unique approach to grow graphene on carbon steel and explore its anti-corrosion application. By introducing Ni element into carbon steel through a laser alloying process to form a Ni/Fe alloy catalyst, we make it feasible to grow graphene on carbon steel. The corrosion rate of graphene covered carbon steel is only 0.05 mm/year, much lesser than that of the stainless steel (0.09 mm/year). The corrosion resistance is up to ~1900 Ω cm^2, which is almost 7 times that of original steel (270.7 Ω cm^2). These results indicate that the *in situ* grown graphene coatings perform very well in resisting harsh environments, much better than stainless steel itself.

1. Introduction

Corrosion is the deterioration of a material as it reacts with its environment. There are various types of environment that are hostile and conducive to corrosion, including fog and humidity, saltwater and alkaline or acidic soils. Therefore, corrosion takes place everywhere and may result in dangerous failures. However, an estimated 25–30% of the annual cost of corrosion can be avoided if optimum corrosion management practices are employed [1,2]. The use of protective coatings is an effective, convenient and economic method. The organic and polymeric coatings are commonly used to separate metallic surfaces from corrosive environments. However, these organic and polymeric coatings are normally highly insulating and also hygroscopic, showing a limited anti-corrosion property. Another approach to enhance the anti-corrosive property is adding alloying elements, which can generate passive oxides to reduce corrosion of the base metal. Owing to its high passivation coefficient (0.74) and its ability to form compact passivation layers, Cr has been one of the most widely used elements to prevent corrosion. This passivated film then protects underlying metal from corrosion. However, the passivated film of Cr is composed of metal and oxygen, while Cl^- ions are highly effective in destroying even stable oxide films. Being a small ion, Cl^- easily penetrates oxide films to corrode the underlying metallic surface. Further, its ability to replace oxygen from the passive oxide surfaces leads to oxide layer dissolution [3–5]. Therefore, it is of strategic significance and economic impact to develop more effective, environmentally friendly and less costly products as alternates.

Graphene is composed of one single layer or few layers of carbon atoms, tightly packed into a honeycomb lattice. It possesses a combination of unique properties, such as high transparency, high electrical conductivity, and excellent chemical impermeability [6–9]. These exceptional properties make graphene an ideal candidate for corrosion inhibition in aircraft and shipping industries. The Nobel Prize Laureate Novoselov K.S. has proposed that the *in situ* grown graphene can be used as a protective coating, owing to its inertness and impermeability [10]. The merit of graphene as anti-corrosion coating is its ability to serve as an ultrathin physical barrier, preventing direct interaction between metals and ambient environment. The anti-corrosion property of graphene has attracted researchers' attentions for years [11–16]. Bunch et al. [9] reported that a monolayer graphene membrane was impermeable to standard gases including helium. This laid the foundation for the use of graphene as a protective coating. Prasai and co-workers [12] reported a detailed study on the anti-corrosion property of chemical vapor deposition (CVD) grown graphene as well as transferred graphene for electrochemical corrosion of Cu and Ni foils. They found that the *in situ* grown multilayer graphene film was corroded

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much slower than the transferred graphene. All these studies demonstrate that graphene is an effective barrier against oxidation or corrosion of metals. However, literatures consist of studies that show shortage of graphene as the anti-corrosion coating. Zhou et al. [13] investigated the long-term oxidation of copper covered by a graphene coating. After 6 months, the graphene-coated copper foil corroded worse than an uncoated foil. Recently, Hsieh et al. [14] reported that the limited protection effect of graphene was caused by structural defects in CVD-grown graphene. They employed atomic layer deposition (ALD) to overcome the defects and obtain better corrosion resistance. All the above works focused on the CVD-grown graphene. In the CVD method, Cu or Ni foils were the most widely-used catalysts for graphene growth. Therefore, the graphene films were used to protect Cu and Ni foils from corrosive environment in those studies. However, the disastrous corrosion mainly occurs in Fe and its relative materials. It is much more significant to investigate the protection of Fe and its related materials by graphene films.

In the present work, we focus on the application of graphene in the metal protection, specially for carbon steels. To meet the requirements of this application, large-area graphene should be grown locally and directly on carbon steel effectively in the open conditions rather than using stand alone heating/gas chambers. We have reported a unique graphene growth approach before [17], utilizing laser irradiation to synthesize large-area graphene with a high rate (28.8 cm^2/min) in the open conditions. This approach offers most of the merits as required, *e.g.* large-area growth, local and direct growth, high efficiency, and in the open condition. The remaining challenge is to grow graphene on Fe substrate. Generally speaking, graphene growth needs specific catalysts, *e.g.* Ru, Ir, Co, Re, Ni, Cu, Pt, Pd [18–21]. Not much has been done on the study of Fe as the catalyst, mainly due to the crystal mismatch between graphene and Fe. The lattice parameter of graphene is 0.246 nm, and the graphene growth favors *fcc* structure, whereas for carbon steel, the main phases are α-Fe (*bcc*) and γ-Fe (*fcc*), whose lattice parameters are 0.286 nm and 0.359 nm, respectively. Besides, C and Fe prefer to form Fe_3C, rather than to grow graphene on Fe. Despite this misfit, several researchers [22–24] have contributed their efforts to growing graphene on steels. John et al. [22] developed a synthesis of graphene on commercially stainless steel foils using direct thermal CVD. They found that the oxide of Mn and Cr along with $MnCr_2O_4$ played a key role in graphene growth. Gullapalli et al. [23] modified carburization process to obtain graphene on stainless steel foils. Although these successful attempts are inspiring, they did not further explore the application of graphene grown on Fe or steel. Secondly, all the reported works were carried out with CVD method, which is a time-consuming approach involving toxic gas emission and high temperature process, and the growth area is largely limited by the chamber size. Further, there is no agreement on the mechanism of graphene growth on Fe catalyst.

Here, we propose a novel approach to grow graphene on normal carbon steel, and even other commercial metals, to realize its capability for metal protection. Since Ni has better catalytic ability than Fe, we introduce Ni element into the carbon steel surface to form a Ni/Fe catalyst with the help of a high power fibre laser. The catalyst was composed of 94.08 wt.% Ni and 5.92 wt.% Fe. The high content of Ni can provide superior conditions for graphene growth. This unique approach overcomes the difficulty of graphene growth on carbon steel. The entire growth processing was implemented in ambient conditions, *i.e.* room temperature and atmospheric pressure, without the use of vacuum chambers. The anti-corrosion property of graphene was analyzed by electrochemical measurement. We confirm that the graphene grown on carbon steel by laser beam can protect the carbon steel from harsh environments, much better than the super stainless steel. This *in situ* formation of graphene on engineering steels by laser approach opens new avenues for the use of graphene in metal protection.

2. Experimental

2.1. Preparation of Ni/Fe catalyst on carbon steel by laser deposition

In this work, the most common carbon steel, 45# steel (GB, equals to 1045# in ASTM), was used as the substrate. The catalyst fabrication is illustrated as following. First, high-purity (99.99%) Ni powders of uniform size, about 75 μm, were assembled into a side shaft powder feeding apparatus (Beijing Aeronautical Manufacturing Technology Research Institute (BAMTRI, http://www.bamtri.com/), DPSF-2). The Ni powders are fabricated with atomization method, provided by BGRIMM (short for Beijing General Research Institute of Mining & Metallurgy) Advanced Materials Science & Technology Co. Ltd. (http://www.bamstc.com/). The melting point of Ni powder is 1455 °C, the density is 1.8–4.8 g/cm^3 and the flowability is ~30 s/50 g. Second, a high power density continuous wave (CW) fiber laser (IPG YLS-2000, wavelength of 1.07 μm, maximum power of 2000 W) was employed to synthesize the catalyst. Before impinging on the surface, the beam is focused to be 0.3 mm in diameter. The power density used was 2.15×10^4 W/cm^2 with a scan rate of 4 mm/s. With the assistance of airflow, the powders were delivered into the laser irradiating area. Almost at the same time, the powders and the substrate were heated and melted by laser irradiation. Then the molten powders and substrate merged together. When the laser moves forward, a Ni/Fe band was formed on the surface. Then, we repeated the above process to fabricate another Ni/Fe band, which partially overlaps with the previous band and the process is repeated. The overlapping ratio of any two adjacent bands was 30%. Varying the powder feeding rate, different catalysts can be fabricated, as shown in Fig. S1. In this paper, we selected one of Ni/Fe catalysts with 94.08 wt.% Ni and 5.92 wt.% Fe for all analysis.

2.2. Graphene growth on Ni/Fe catalyst by laser irradiation

Upon laser alloying process, the surface was polished mechanically. The nano carbon powder (size of ~50 nm) was mixed with alcohol (analytical reagent) to form a paste (1.0 g carbon powder with 1.6 ml alcohol). The nano carbon powders are fabricated by high-energy ball milling, provided by Beijing Research Institute of Powder Metallurgy Co. Ltd. (http://www.beifenco.com/). The melting point of carbon powder is 3850 ± 50 °C and the density is 0.78 g/cm^3. With a spin coater, a 14 μm thick carbon coating was evenly coated on the polished surface. The same fiber laser was again employed to scan the pre-coated carbon source on the Ni/Fe substrate. When the laser was shut off, graphene was grown locally. The laser power density was 14.1×10^3 W/cm^2, and the scanning rate was 60 cm/min with 25 L/min argon (99.99%) as shielding gas.

2.3. Electrochemical corrosion measurement

3.5% NaCl aqueous (aq) solutions was designed to imitate the seawater. The corrosion resistance was investigated by an electrochemical measurement system. The reference electrode was the saturated calomel electrode (SCE) in a Luggin capillary, and the auxiliary electrode was platinum (Pt) electrode. The measurements were implemented in a 500 ml beaker at room temperature, and the distance of Luggin capillary and working electrode was 2–4 mm. The polarization curves were obtained by sweeping the voltage from −900 to +500 mV with a scan rate of 1.0 mV/s