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Multilayer Graphene: A Potential Anti-oxidation Barrier in Simulated Primary Water

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Multilayer graphene as a potential anti-oxidation barrier to protect nickel foils from oxidation was studied in simulated primary water of pressurized water reactors (PWRs). The results show that after immersion for 1000 h, the structure of the multilayer graphene remains unchanged and no obvious oxide film formed on the graphene coated nickel foils, indicating multilayer graphene can effectively act as the anti-oxidation barrier to protect the substrate from oxidation and hence can improve the heat transfer efficiency of the substrate in simulated primary water of PWRs.

KEY WORDS: Graphene; Raman spectroscopy; X-ray photoelectron spectroscopy; Anti-oxidation barrier; Simulated primary water

1. Introduction

In pressurized water reactors (PWRs), nickel-based alloys are now widely used to fabricate tubes in steam generators (SGs) due to their good corrosion resistance[1]. However, oxide films which play a crucial role in stress corrosion cracking and crack propagation can be formed on the tube surfaces during service[2]. In addition, the oxide films on the surface can decrease the heat transfer efficiency of the tubes, which correspondingly increases the cost of management and operation of the nuclear power plants[3]. In order to protect metal surfaces from oxidation, many approaches, such as organic layers[4−6], inorganic coatings[7], paints[8,9], and polymers[10,11] have been developed. However, these coatings are not suitable to be used in PWRs as protective barriers. Is there any effective barrier to protect the materials in PWRs?

Graphene, a monolayer of carbon atoms tightly packed into a honeycomb lattice, is being widely studied across the whole world due to its unique structure and properties[12,13]. Four properties have determined graphene to have the potential as a good anti-oxidation barrier in PWRs. Firstly, graphene on the substrate can act as a barrier to provide a physical separation between the substrate and reactants[14]. By creating an air-tight "balloon", Bunch et al.[15] have demonstrated that a monolayer graphene is impermeable to standard gases including helium. Secondly, graphene is chemically inert and is stable in high temperature air[14,16,17] or under conditions where other substrates will undergo rapid chemical reactions[18−24]. Chen et al.[14] have proved that graphene can not only be stable when heated to 200 °C in laboratory air for 4 h or immersed into a solution of 30% (weight/weight) hydrogen peroxide up to 45 min but also act well to prevent the substrates from oxidation. Thirdly, the wettability of the substrate is independent of the number of layers of graphene sheets and the interaction between the substrate and overlying water can be in the same way as in the absence of graphene, indicating graphene barrier is especially suitable for SG heat transfer tubes[25]. Fourthly, the room temperature value of the thermal conductivity of a single-layer graphene is $\sim 5 \times 10^3$ W/(m K), about ten times higher than that of copper[26], indicating the graphene barrier is advantageous for improving the heat transfer efficiency of SG tubes.

In addition, many methods[27−30] have been developed to produce high quality graphene in mass production. To date, by using chemical vapor deposition (CVD), large area, monolayer or multilayer graphene can be synthesized on different substrates including Pt[31], Ni[32−34], Cu[27], Pd[35], Ru[36], Ir[37] and even stainless steels[38]. Graphene layers can also be transferred to any arbitrary substrate by using various kinds of transfer methods[39−44], which makes graphene being protective barriers possible.

2. Materials and Experimental Methods

Since the methods of synthesizing graphene on nickel have been technologically matured[32−34], in this work, nickel foils

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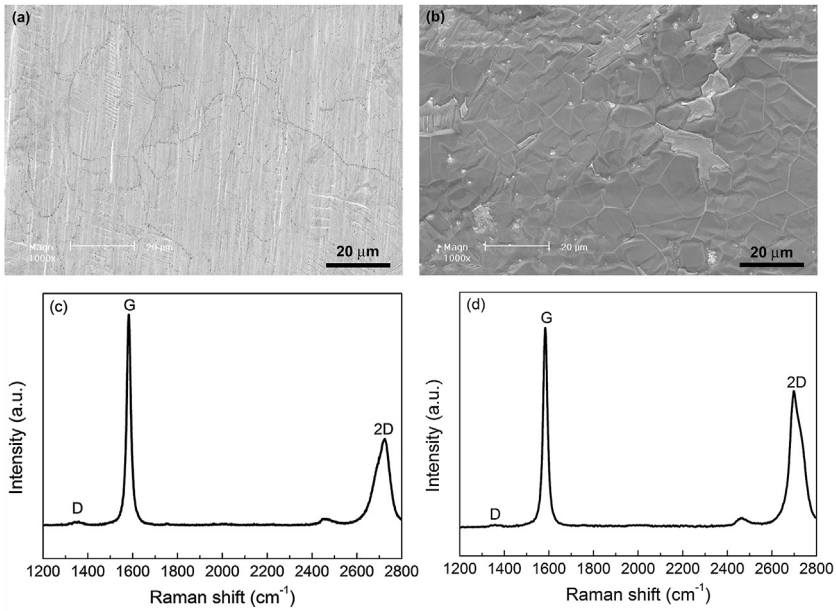

Fig. 1 SEM images of the Ni (a) and the G/Ni (b) samples before immersion. Raman spectra of the gray area (c) and the light-gray area (d) of the G/Ni sample (b).

were selected as substrate. Graphene coated nickel foils (labeled as "G/Ni") and uncoated nickel foils (99.99% Ni, labeled as "Ni") were purchased from XIAMEN G-CVD MATERIAL TECHNOLOGY CO., LTD (China). The graphene was synthesized on nickel foils by CVD. The general CVD process was: argon was introduced into the quartz tube before and after the nickel foils were put into; the nickel foils were heated at 1050 °C under a 20 sccm (standard cubic centimeters per minute) flow of hydrogen for 35 min; then hydrogen and methane both at a flux of 10 sccm were introduced into the tube at 1050 °C for 80 min; the tube was cooled to 450 °C; argon was introduced into the quartz tube again until the tube was cooled to room temperature. Multilayer graphene (4−10 layers) can be synthesized on the nickel foils by using this method.

The immersion test was performed in a 1.4 L 316L-type autoclave. The simulated primary water of PWRs was 1500 ppm (by weight) B as H_3BO_3 and 2.3 ppm (by weight) Li as $LiOH \cdot H_2O$. Before elevating the temperature, the simulated primary water was deaerated by continuous bubbling with pure nitrogen gas (99.99%) for 4 h. The temperature of the immersion test was 300 °C and the immersion time was 1000 h.

The Ni and G/Ni samples were characterized by scanning electron microscopy (SEM, FEI XL30), Raman spectroscopy (Jobin-Yvon Labram HR 800) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) before and after immersion.

3. Results and Discussion

The surface morphology of the Ni sample is shown in Fig. 1(a). Grain boundaries, dotted inclusions along the grain boundaries and rolling indentations are obvious. Although it is very difficult to observe the monolayer graphene by SEM as the ultra-low secondary electron emission of graphene[45], SEM graph of G/Ni sample in Fig. 1(b) clearly shows the morphology of the multilayer graphene. The nickel foil is thoroughly covered by multilayer graphene and this multilayer graphene is obviously composed of gray areas and light-gray areas.

The typical Raman spectra of the gray areas and the light-gray areas in Fig. 1(b), much similar to the results in Refs.[32,34], are shown in Fig. 1(c) and (d), respectively. Only two major peaks exist: G band around 1580 cm^{-1} and 2D band around 2700 cm^{-1}[29]. Sometimes, D band around 1350 cm^{-1} which reveals the defects of the graphene can also be found in the Raman spectra[46]. The ratio of integrated intensity of the G band to the 2D band is usually used to estimate the number of layers of graphene[47]. Here the I_G/I_{2D} ratio of the gray areas is about 2.3, indicating that the gray areas are covered by multilayer graphene (6−10 layers)[32]. In addition, the I_G/I_{2D} ratio of the light-gray areas is about 1.4, less than 2.3, indicating that the light-gray areas are also covered by multilayer graphene (4−5 layers)[19], but the number of layers is less than that of the gray areas. Besides, the multilayer graphene is in high quality since no obvious D band is found in both of the areas.

The morphologies of the Ni and G/Ni samples after immersion for 1000 h in the simulated primary water of PWRs are shown in Fig. 2(a) and (b). The Ni sample is thoroughly covered by filamentous oxides (Fig. 2(a)), while no obvious oxide films can be observed on the G/Ni sample (Fig. 2(b)), indicating multilayer graphene can effectively act as the barrier layer to protect the substrate from oxidation. Small oxide particles which are rich in Fe, Ni and O, surrounded by the dashed circles in Fig. 2(b), can be observed on the G/Ni sample after immersion for 1000 h. These small oxide particles are formed on the surface by redeposition. Ni may come from the Ni samples and Fe comes from the inner wall of the autoclave. The Raman spectra of the gray areas and light gray areas on the G/Ni sample after immersion for 1000 h (Fig. 2(c) and (d)) are very similar to that before immersion (Fig. 1(c) and (d)), revealing that the structure of the multilayer graphene remains unchanged after a 1000 h immersion in the simulated PWR primary water. No peak can be found in the Raman spectra of the Ni sample before oxidation, while NiO peak (550 cm^{-1})[48] can be clearly observed on the Ni sample after immersion for 1000 h in the simulated primary water of PWRs (Fig. 3).