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Investigations of low-energy ion irradiation influence on glassy polymeric carbon

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Abstract

Glassy polymeric carbon (GPC), which is made from phenolic resins, has a high chemical inertness and is used as high temperature and radiation resistant coatings, as high temperature heat-exchangers, as well as a biomaterial in medicine for the manufacture of heart valves and prosthetic devices [G.M. Jenkins, D. Ila, H. Maleki, Mater. Res. Soc. Symp. Proc. 394 (1995) 181]. GPC is also used for the harsh environment of space, as well as for protective coating against extreme environments such as high temperature, highly ionizing radiation, as well as corrosive environments.

In this work, we present the results of our investigation of the influence of the low-energy ion irradiation in glow-discharge plasma on GPC.

Chemical changes in GPC prepared at 1000 °C were studied using FTIR, micro-Raman spectroscopy and Rutherford backscattering spectrometry (RBS). Porosity changes were monitored through introducing lithium from a molten LiCl salt into GPC and using the (p,α) nuclear reaction analysis (NRA) to measure Li concentration in treated GPC.

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Keywords: Glassy polymeric carbon; Low-energy ion irradiation

1. Introduction

Glassy polymeric carbon (GPC) is made from cured phenolic resins by heat treatment in inert environment. During the heat treatment temperature chemical changes take place and eliminate non-carbon elements by diffusion while aromatic rings condense to form graphitic lamellar layers. The final structure of GPC is composed of these graphitic layers in random arrangement with unconnected pores between them. The material appears dark, hard and vitreous [1,2].

Fig. 1(a) shows the chemical structure of resol, a combination of phenol and formaldehyde units [3]. Low temperature heat treatment, below 500 °C, will combine these units to form an intermediate structure similar to the short link shown in Fig. 1(b). Further heat treatment at higher temperatures will increase the dehydrogenation and result in cross linking of polymer chains forming a branched three-dimensional network of pure carbon which is an interconnected aromatic network of pure carbon, as illustrated in Fig. 1(c).

Plasma treatment is a well-known process which is used for surface modification of polymers. The process consists of chemical and (or) structural change phases of the polymer surface. After the polymer ion exposure the following changes can be observed: new bond formation, bond

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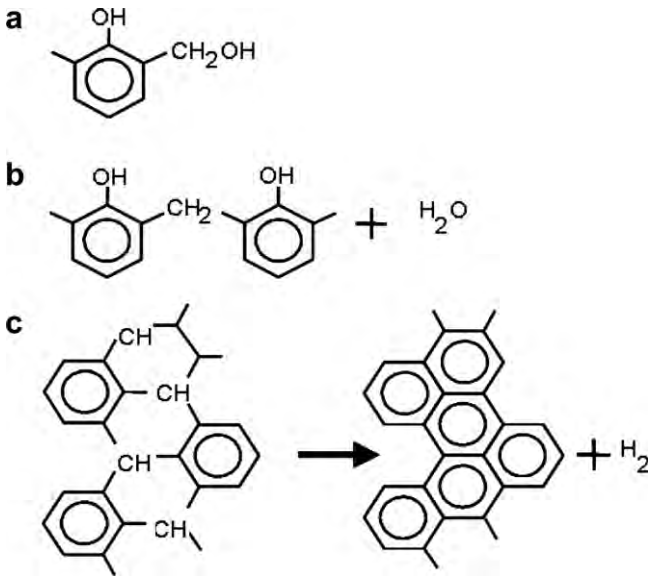

Fig. 1. (a) Structure of phenyl formaldehyde resin unit. (b) Low temperature heat treatment expels water and forms a branched structure of a short polymer chain. (c) High temperature heat treatment expels hydrogen and forms a branched 3D network of pure carbon [2].

opening, gas emission, radiation oxidation, polymer crystallinity changes, etc. Changes caused by ion irradiation that take place in polymers are defined by the phase condition of a polymer (crystalline or amorphous), by the irradiation temperature, the presence of damp, oxygen and other impurities in polymers [4].

This investigation was conducted to investigate the influence of low-energy irradiation in glow-discharge plasma on the GPC polymer and to study the material modification caused by ion irradiation.

2. Experimental methods

GPC samples were prepared from liquid resol $C_7H_8O_2$ precursor in accordance with procedures established in [2,5] and pyrolized at 1000 °C.

Samples were placed in a specially constructed plasma generator and were exposed to glow-discharge plasma by ions of the residual gases of the vacuum. The ion energy depended on the voltage applied to the plasmatron and did not exceed 0.5–1.5 keV. Irradiated fluence was 2×10^{17} ion/cm^2. The temperature in the chamber was controlled during the irradiation process and did not exceed 343 K while the irradiation time varied from 100 to 150 min.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements were performed using a Tensor 27 spectrometer with a Pike-ATR accessory equipped with ZnSe crystal. Raman spectra were acquired using a LabRam spectrometer with a He–Ne laser wavelength $\lambda = 632$ nm.

We used Rutherford backscattering spectrometry (RBS) with a 2.1 MeV He^+ beam to study elemental constituents in the GPC samples as well as nuclear reaction analysis (NRA) to observe porosity changes after the low-energy ion irradiation. For this purpose samples were immersed for 1 h at 700 °C in a molten lithium chloride bath. Subsequently, a 1 MeV proton beam and the $Li^7(p,\alpha)$ reaction were used to experimentally measure the porosity. The yield of the $Li^7(p,\alpha)$ reaction was observed 6 μm deep into the surface of both non-irradiated and irradiated samples by low-energy ions.

3. Results and discussion

After irradiation in glow-discharge plasma, GPC samples were examined and compared with a non-irradiated sample to detect the influence of low-energy ion irradiation on GPC characteristics.

Fig. 2 shows the attenuated total reflectance (ATR), FTIR spectra of non-irradiated (curve 1) and irradiated GPC (curves 2 and 3). Spectra of irradiated samples show CH bonds formation that may occur as a result of the aromatic ring breaking.

Fig. 3 shows Raman spectrum of non-irradiated GPC prepared at 1000 °C. The dotted curve represents the data obtained from Raman spectrometer. A Lorenz equation and five peaks (hatch curves) were used to fit the data. Two regions of interest (D- and G-line) using Raman spectrometry were studied. The G-line is attributed to graphene structure formation in the material [6] and observed at the wave number of 1600 cm^{-1}. The D-line observed at 1326 cm^{-1} is attributed to amorphous structure, 'disorder' in the material, as well as the vibration of the bond at the

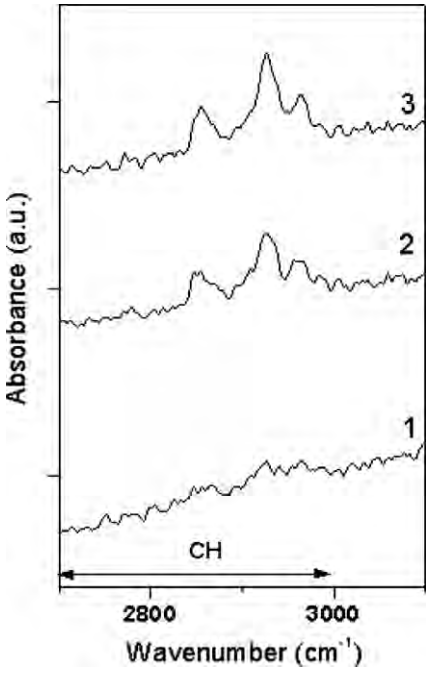

Fig. 2. ATR-FTIR spectra of GPC prepared at 1000 °C: 1 – non-irradiated sample, 2 – sample irradiated at 1.5 kV for 100 min and 3 – sample irradiated at 0.5 kV for 150 min.

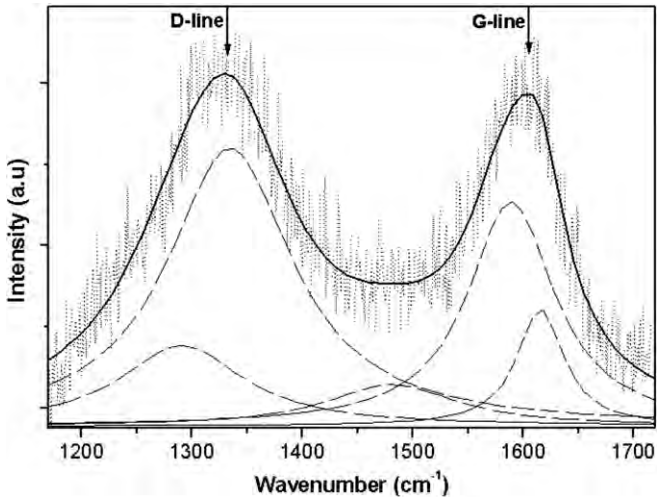

Fig. 3. Raman spectrum of non-irradiated GPC prepared at 1000 °C.

Table 1
D/G ratio for GPC samples

GPC sample	D/G ratio
Non-irradiated	1.082 ± 0.005
Irradiated at 0.5 kV for 150 min	1.051 ± 0.008
Irradiated at 1.5 kV for 100 min	1.034 ± 0.009

edge of the graphitic ribbons. The D/G ratio for non-irradiated and irradiated samples as well as the measurement error are given in Table 1.

According to Table 1 D/G ratio decreases with the increase in ion energy. This corresponds to the increase in crystallinity part, an 'ordering' process on the GPC surface after low-energy ion irradiation.

Fig. 4 shows lithium concentration profile obtained by NRA. Irradiated samples (graphs 2 and 3) revealed 10^4 less

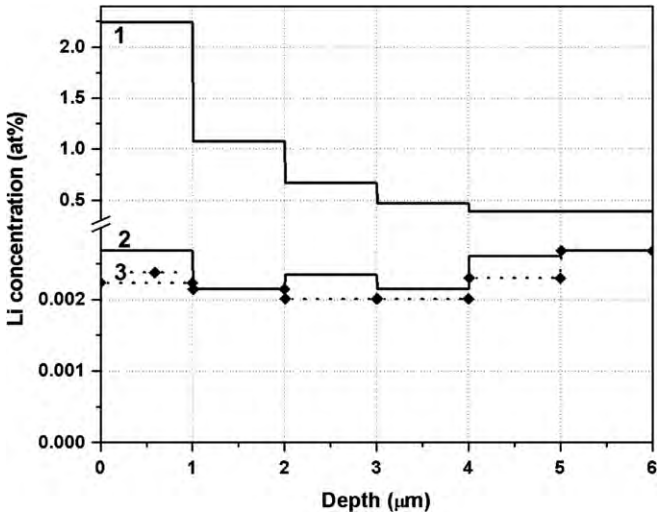

Fig. 4. Comparison of lithium profile of GPC prepared at 1000 °C: 1 – non-irradiated sample, 2 – sample irradiated at 1.5 kV for 100 min and 3 – sample irradiated at 0.5 kV for 150 min.

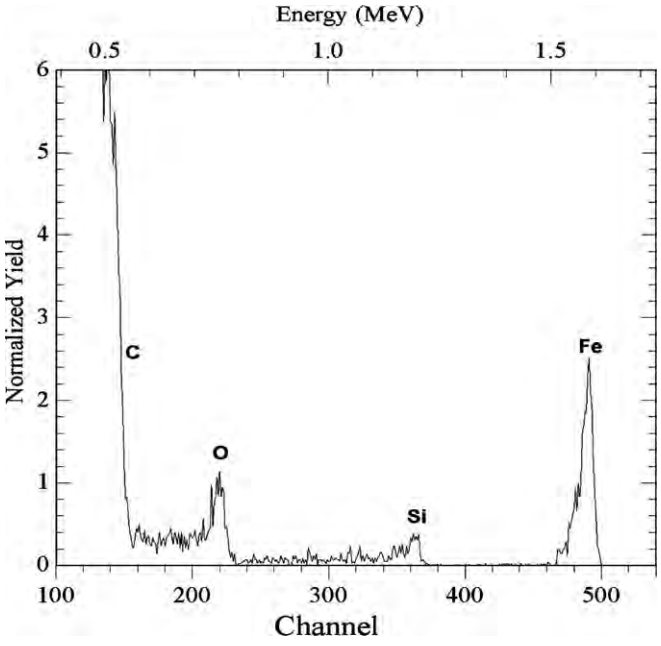

Fig. 5. RBS spectrum of GPC sample irradiated at 1.5 kV for 100 min.

lithium concentration in comparison with the non-irradiated sample (graph 1). Thus, after the low-energy ion exposure the decrease in porosity is observed. The latter can be used according to functionality of the polymer. The result obtained by NRA proves to be well correlated with Raman measurements (Table 1).

We used RBS to study the isotopic and elemental content of samples before and after irradiation. The RBS spectrum of irradiated GPC (Fig. 5) shows iron on the surface in comparison with non-irradiated sample, perhaps occurred from the plasma generator cathode as a result of a secondary emission process. So after irradiation the sample surface has a layer consisting of GPC components and iron. A RUMP simulation indicates that a 0.05 μm surface layer has an iron concentration of 2% that cannot influence significantly on porosity measurement.

4. Conclusions

Low-energy ion irradiation in glow-discharge plasma of GPC leads to decrease in porosity and amorphous part and to new CH bond formation. Such kind of modification may find practical application according to GPC functionality.

Acknowledgments

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