Modification of oxidized graphite edge surface with poly(vinyl chloride)

M. NAKAHARA
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

S. ASAI, Y. SANADA
Centre for Advanced Research of Energy Technology, Hokkaido University, N-13, W-8, Sapporo 060, Japan

T. UEDA
Advanced Technology Research Centre, Mitsubishi Heavy Industries Ltd, Kanazawa-ku, Yokohama 236, Japan

An oxidized edge surface of pyrolytic graphite (PG) has been prepared by electrochemical treatment. A thin layer of poly(vinyl chloride) (PVC) was coated on the oxidized edge surface, and the PVC-coated sample heat treated at 300, 400, and 500 °C, respectively. The influence of the PVC coating on the structural change of the oxidized edge surface of PG caused by the heat treatment was studied by laser Raman and Fourier transform–infrared attenuated total reflection spectroscopies. For the electrochemical treatment, the formation of oxygen-containing functional groups proceeds over the edge surface of PG. With increasing degree of oxidation, the functional groups are formed in the following order: hydroxyl groups, carboxyl groups, lactone groups, quinones, and acid anhydrides. Acid anhydrides are formed on the outermost surface and completely eliminated by heat treatment up to 300 °C. The other functional groups remain even after heat treatment up to 500 °C. However, the functional groups are eliminated by the PVC coating, the elimination temperature depending on the type of functional groups: quinones, lactone groups, and carboxyl groups are eliminated at 300, 400, and 500 °C, respectively. PVC coated on the edge surface is found to play an important role in the complete elimination of oxygen-containing functional groups with \( > \text{C}=\text{O} \) through heat treatment at 500 °C.

1. Introduction
Carbon fibre-reinforced carbon (C/C) composite has been developed for high-temperature resistant and light structural material and has potential for application to space vehicles. In application, an appropriate protection system against high-temperature oxidation is required for the C/C composite. Silicon carbide (SiC) coating is well known as a modification technique for the composite surface [1, 2]. However, the structural non-uniformity of the composite surface disturbs the uniform coating of the SiC film.

Ueda et al. [3] found a novel protection system: an additional carbon layer, which bonds tightly to the surface of the C/C composite, is introduced to the composite system. They demonstrated that a strong bonding between the carbon layer introduced and the composite can be obtained by thermal decomposition of poly(vinyl chloride) (PVC) as an interlayer material between the carbon layer and the composite. However, the strong bonding mechanism of the carbon layer over the composite surface is unknown.

In order to clarify the phenomena occurring in the interface, the oxidized edge surface of pyrolytic graphite (PG) is used as the composite model surface. In this work, the effect of PVC coating on the composite model surface was investigated by spectroscopic analyses.

2. Experimental procedure
Mirror-polished edge surfaces of PG (Tomoe Engineering) [4], which are parallel to the c-axes of graphitic crystallites, were prepared for use as a model of active surfaces of C/C composites. The surfaces were ultrasonically rinsed in acetone and distilled water, successively, and then dried at 100 °C for 20 min in an oven.

In order to introduce oxygen-containing functional groups to the edge surface, electrochemical treatment was carried out with 0.1 m ammonium hydrogen carbonate solution; the specific electric charge (electric charge, C, per unit area m²) was \( 4 \times 10^5 \text{ Cm}^{-2} \). After surface treatment, the surfaces were rinsed in distilled water and dried at 100 °C for 20 min in the oven.

The electrochemically treated edge surfaces were coated with PVC by the following procedure. The surfaces were soaked in a tetrahydrofuran (THF) solution containing 2.5% PVC by weight for 30 min. After
soaking, the surfaces were again dried at 100°C for 20 min in the oven.

PVC-coated and uncoated samples were heat treated under an argon gas stream at the following temperatures; 300, 400, and 500°C. After attainment of the given temperatures, the samples were allowed to cool immediately.

The samples thus prepared were analysed by using Fourier transform infrared–attenuated total reflection (FTIR–ATR) technique [5] with respect to surface functional groups and interfacial interaction between the thin layer of PVC and the edge surface of PG. An FT–IR system 800 (Nicolet Japan) with a model-9 ATR attachment (Wilks Scientific) was used to measure FTIR-ATR spectra. The resolution of absorption spectra was 4 cm⁻¹, signals of 200 scans being collected. The change of graphitic structure of the edge surfaces after heat treatment was estimated by laser Raman spectroscopy. Raman spectra of the surfaces were measured by using the RAMALOG-10 system (SPEX). The 514.5 nm of an argon-ion laser (200 mW) was used to induce the Raman spectra. The details of the measurements are described elsewhere [4].

3. Results and discussion
Fig. 1 shows the ATR spectrum of an edge surface electrochemically treated at \(4 \times 10^5\) C m⁻². Absorption of oxygen-containing functional groups is clearly marked in the range 1900–1500 cm⁻¹. The range can be divided into five regions, A–E, as shown in Fig. 1. Absorption bands in Regions B, C, and E can be assigned to the C=O stretching vibrations of lactone and carboxyl groups, and C=C stretching vibrations of aromatic rings conjugated with a carbonyl group, respectively [6]. We have already reported that the main absorption bands appear in Regions B, C, and E for the specimens electrochemically treated over the range 5000–50 000 C m⁻² [6].

On increasing the specific electric charge from \(5 \times 10^4\) C m⁻² to \(4 \times 10^5\) C m⁻², new absorption bands appear clearly in the Regions A and D. An absorption band in Region A can be assigned to acid anhydrides [7]. On the other hand, an absorption band in Region D can be assigned to carbon–oxygen stretching vibrations induced by hydrogen bonds, as shown in Fig. 1 [7].

Fig. 2a shows the relation between the R-value and the extent of electrochemical oxidation for the edge surface of PG. The R-value is the intensity ratio of the G band (1585 cm⁻¹ band) to the D band (1360 cm⁻¹ band) [8] and is a function of the crystallite size, \(L_a\) [9]. Taking account of the R-values for the pristine specimen (\(L_a = 10\) nm) and for the oxidized one (\(L_a = 2.6\) nm), surface graphitic structure treated at \(4 \times 10^5\) C m⁻² undoubtedly becomes disordered.

It seems that acid anhydrides are introduced to the edge surface, when the edge surface structure is dramatically destroyed. In this case, because absorption in Region D also occurs at the same time, oxygen-containing functional groups present on the edge surface would form hydrogen bonds to acid anhydrides. From previous studies, the following facts are clarified. (i) Mild treatment, which does not induce the destruction of edge surface structure, introduces hydroxyl groups to the edge surface [4]. (ii) When the surface structure is destroyed, carboxyl groups are introduced to the surface [4]. (iii) The ratio of lactone groups to carboxyl groups increases with the electrochemical treatment level [5]. In addition, absorption due to quinones increases markedly on severe treatment, \(5 \times 10^4\) C m⁻² [6]. Judging from these facts, the oxidation of the edge surface would result in the