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Carbon deposition by electrolytic heating of a water–ethanol solution

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A new approach was undertaken to deposit carbon from organic solutions. The method consisted of discharge-heating a tungsten cathode in a water-ethanol electrolyte under a high d.c. voltage. At high temperatures the cathode was covered with a sheath of vapour. In the low voltage region, no carbon deposition occurred. Instead, an uneven surface with spikes of tungsten or a relatively smooth surface, which evolved with increasing voltage, were observed. High voltages and high concentrations of ethanol were favourable for the deposition of bulky carbon and also for the carburization of tungsten to WC. Glassy carbon and disordered graphitic carbon were obtained at the highest applied voltages.

1. Introduction

Diamond film formation by chemical vapour deposition requires at least three factors: a carbon source, atomic hydrogen and a high substrate temperature [1]. Carbon is usually supplied from methane. Atomic hydrogen is generally produced by the decomposition of a hydrogen molecule with a hot filament [2] or in a plasma [3]. Another way of supplying atomic hydrogen is by electrolysis. The idea of supplying the nascent state hydrogen in this manner led to our previous attempt at carbon deposition by the electrolysis of a water–ethylene glycol solution [4]. This resulted in graphitic carbon deposition on the silicon cathode at temperatures lower than 120 °C. Thus, our next step was to carry out similar research with a higher temperature cathode. We now report on preliminary experiments of carbon deposition by the electrolytic heating of organic solutions.

Electrolytic heating of an immersed electrode is known as contact glow-discharge electrolysis [5] when attention is paid to chemical reaction in the solvent [6]. To our knowledge, no carbon deposition by this process has been documented in literature. However its application to technological areas such as carburization [7] and sintering [8] has been reported.

2. Experimental procedure

The experimental arrangement for electrolytic heating is shown schematically in Fig. 1. The solution was circulated with a pump and cooled with the aid of a cooling bath. A reservoir was necessary to compensate for the loss of solution from vaporization. The liquid temperature was measured in the reservoir by a thermocouple. The main cell was a 300 ml beaker. Using a tungsten, platinum or carbon wire anode, anodic discharge-heating was investigated. It did occur over short time periods but the hot anode eventually melted. Thus, cathodic electrolytic heating was examined. The anode was made of four graphic rods placed at a distance of 25–28 mm from the central cathode. The cathode was a tungsten wire of 0.5 mm diameter or a tungsten plate of 5 × 5 × 0.3 mm. The tip of the tungsten wire was immersed 5 mm into the solution. The tungsten plate was bound with a tungsten wire of 0.3 mm diameter and the whole plate was immersed. An inert atmosphere of argon or nitrogen was fed into the cell to prevent oxidation of the tungsten during the electrolytic heating. It served also to prevent the accumulation of hydrogen and oxygen in the gaseous atmosphere with its possible risk of explosion. After several arbitrary trials with aqueous solutions of methanol, ethanol, i-propyl alcohol, glycerol, ethylene glycol, acetone, acetic acid, formic acid and sucrose, ethanol was chosen for detailed investigation. The water–ethanol system was one of the apparently high yield systems producing black deposits on the tungsten wires. The electrolyte was prepared using deionized water and contained a constant concentration of 0.1 mol % potassium acetate. The tungsten plate temperatures were estimated using an optical pyrometer. The experiment was carried out under atmospheric pressure. After the electrolytic heating, the specimen was dipped in hot water for 10 min and then examined by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) using CuK$_\alpha$ radiation, electron probe microanalysis (EPMA) and Raman spectroscopy. The 514.5 nm line of an Ar-ion laser was used to induce the Raman spectrum.

3. Results and discussion

3.1. Voltage–current characteristics

Fig. 2 shows a typical voltage–current curve obtained with a 30 mol % ethanol electrolyte with a tungsten

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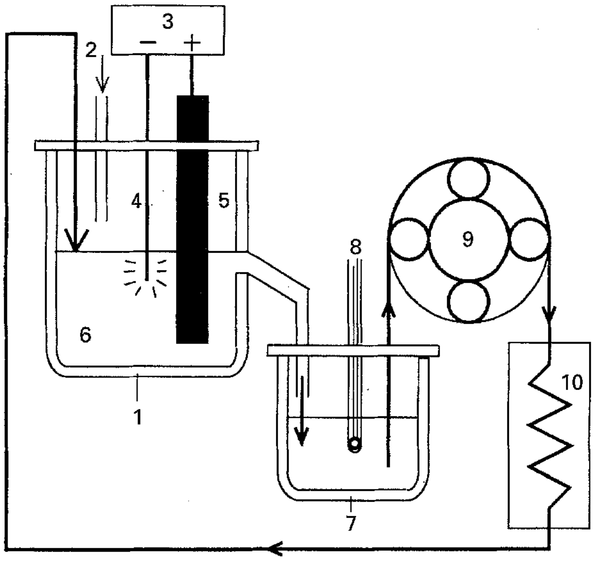

Figure 1 Schematic illustration of the experimental arrangement: (1) main cell, (2) argon or nitrogen, (3) d.c. source, (4) tungsten cathode (wire or plate), (5) graphite anode, (6) electrolyte, (7) reservoir (8) thermocouple, (9) pump, (10) cooling bath.

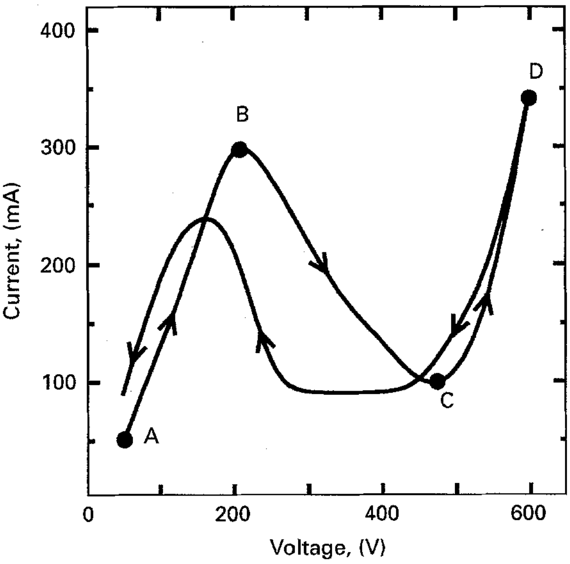

Figure 2 Characteristic voltage–current curve of a 30 mol % ethanol solution using a wire cathode: AB conventional electrolysis, BC electrolysis–discharge transition, CD electrolytic heating.

wire cathode. In the low voltage region AB, conventional electrolysis occurred. At the point B, intense bubbling was accompanied by a small flash of pale blue light at the cathode. Between B and C, the current fluctuated violently. In the high voltage region CD, the cathode was surrounded by a vapour sheath and the discharge through the sheath was relatively stable. The luminosity changed from pale blue to orange and on to blinding white with increasing voltage. It was even possible to melt the tungsten wire ($T_m = 3400\,^{\circ}\mathrm{C}$) with higher voltages. On decreasing the voltage, the electrolytic heating weakened and the conventional electrolysis recurred at a voltage lower than the initial point B. The heating mechanism is thought to be due to a voltage drop in the discharge occurring close to the metal surface of the cathode, and this may result in thermoionic emission from the cathode and very high currents [5].

3.2. Tungsten wire

Firstly, systematic observations were made to see the effects of voltage and concentration on the electrolytic heating of tungsten wire. Heating was carried out at a constant voltage for 30 min. Fig. 3 shows SEM images of samples treated in a 30 mol % ethanol solution. The wire was uneven and irregular at 400 V (Fig. 3a) and spikes of tungsten were observed as identified from EPMA studies. It may be sputtered tungsten electrodeposited on the cathode. At 450 V (Fig. 3b), the surface was relatively smooth with no apparent deposit. EPMA examination of a 500 V sample (Fig. 3c) revealed that an uneven carbon film with holes was deposited. The 550 V sample (Fig. 3d) showed a black bulky carbon deposit.

Fig. 4 summarizes the surface morphology and carbon deposition from 1–50 mol % ethanol solutions. At voltages lower than 400–500 V with 15–50 mol % ethanol or in less than 10 mol % ethanol, the wires were sputtered and no carbon deposition occurred. The surface was either uneven with spikes of tungsten or relatively smooth. In contrast, in the region ① where high voltage of 550–650 V are applied to solutions containing more than 30 mol % ethanol, bulky carbon was obtained. Holes were frequently observed in the carbon films deposited in the narrow region ②. A higher applied voltage gave a higher liquid temperature and hence larger evaporation of solution. However, the former did not exceed 50 °C and the latter was less than 50 ml. The liquid colour remained unchanged. The electric power was 60–180 W and the current density was 1.6–3.8 $\mathrm{A\,cm^{-2}}$. The high current density is comparable to that of chemical vapour deposition by the d.c. plasma method [10] where diamond or glassy carbon grows surrounded by a positive column.

With higher voltages than that marked in Fig. 4, the wire tip was rounded or its length diminished and often the bulky carbon deposit disappeared leaving dispersed carbon films. Raman spectra of the samples prepared under such extreme conditions are given in Fig. 5. The treatment in 40 mol % ethanol under 900 V for 18 min yielded glassy carbon (Fig. 5a). The black deposits from 100 % ethanol treated with 1240 V for 30 min were identified [9] as disordered graphitic carbon (Fig. 5b).

3.3. Tungsten plate

The electrolytic heating of the tungsten plate was then examined. The heating was carried out at a constant voltage for 30 min. Fig. 6 shows the carbon deposition and the relative amounts of resulted phases as roughly judged from the XRD patterns. XRD peaks from tungsten were not considered, because they always appeared even after the fastening wire had been removed. It is clearly demonstrated that the voltage, required for effective electrolytic heating, increased with increasing ethanol concentration. A relatively

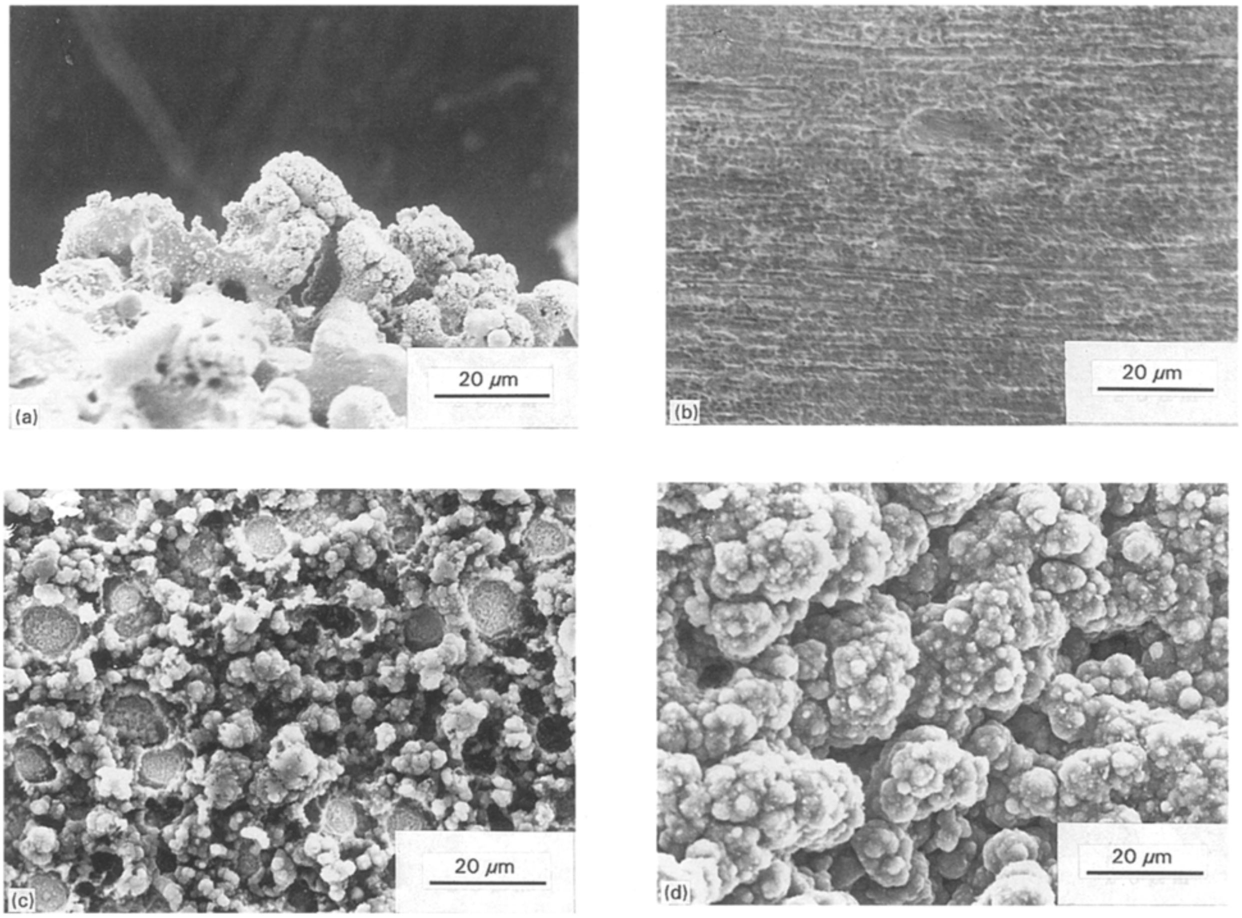

Figure 3 SEM images of treated wire in a 30 mol % ethanol: (a) rugged surface with spikes of tungsten at 400 V, (b) relatively smooth surface at 450 V, (c) uneven carbon film with holes at 500 V, (d) bulky carbon at 550 V.

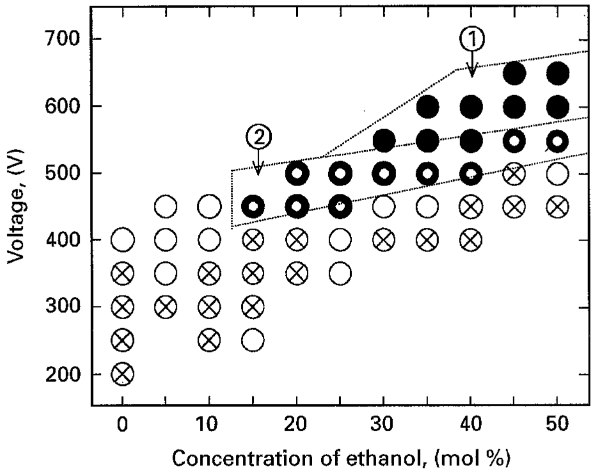

Figure 4 Morphology and carbon deposition on wire as a function of concentration and voltage: (⊗) spikes of tungsten, (○) smooth surface, (◉) uneven carbon film with holes, (●) bulky carbon.

large amount of black carbon was deposited in region ① in the form of films on the flat surface and often as bulky carbon at the corners. The carbon was the dominant phase and it was accompanied by smaller concentrations of WC and W_2C. It is probable that the carburization occurred first and then the carbon deposition took place on the carbides. Region ② is the carburization region where WC is observed in greater concentrations than W_2C. In region ③, the carburiz-

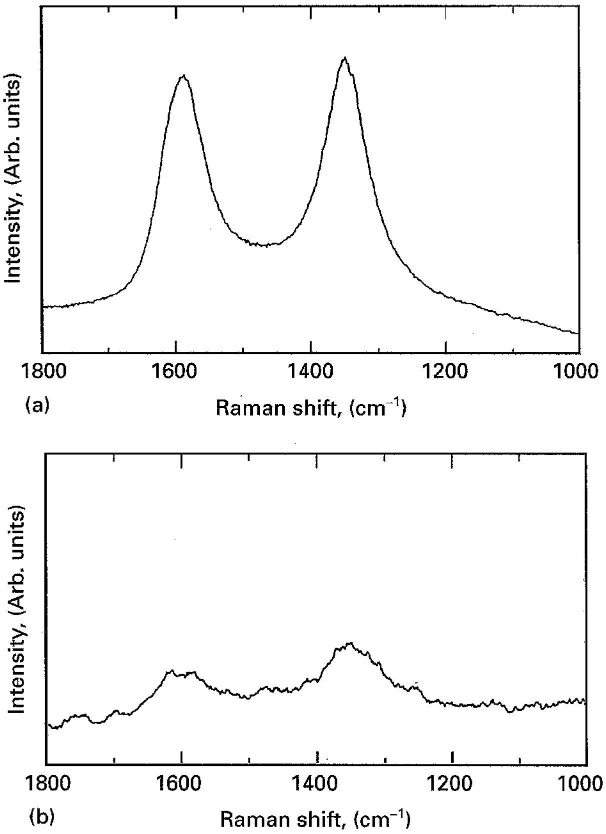

Figure 5 Raman spectrum of deposited carbon on wire: (a) 900 V for 18 min in 40 mol % ethanol, (b) 1240 V for 30 min in pure ethanol.

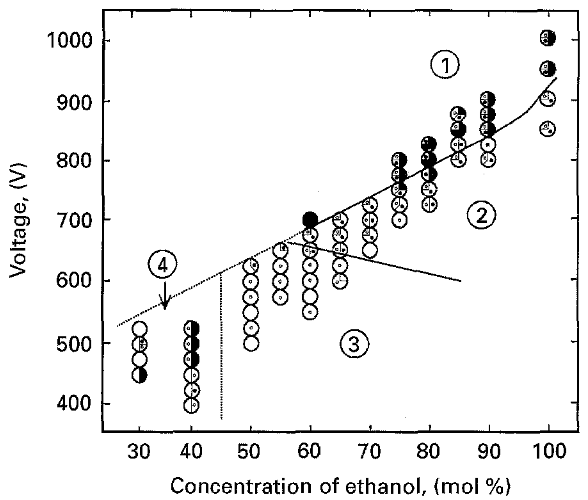

Figure 6 Relative amount of carburization and carbon deposition on plate: (○) no change, (◎) W_2C, (⊙) WC, (●) carbon.

ation also occurred, but here, the amount of W_2C was larger than that of WC.

Although the specimens were not in thermal equilibrium, the fact that WC prevailed over W_2C at high concentrations of ethanol seems to reflect the equilibrium phase diagram. The W–C system [11] predicts mixtures of WC and C for $C \geqslant 50$ at %, W + W_2C for $C \leqslant 33$ at % and $W_2C + WC$ in-between above 1250 °C. The W_2C phase disappears below 1250 °C. No particular dependence of the treatment on voltage was observed in region ④. The plate temperatures at the highest voltage indicated in Fig. 6 for 40, 60, 80 and 100 mol % ethanol varied between 900–950, 1800–1900, 1100–1300 and 1000–1040 °C, respectively. However, these temperatures should be regarded as mere estimates, because the pyrometer was always adjusted to the value of tungsten emissivity and no correction was made on the carbon deposition. Further, the liquid colour blackened. The maximum liquid temperature, evaporation loss, power and current density corresponding to the above composition and voltage were 54–66 °C, 100–350 ml, 200–800 W and 0.8–2.4 Acm^{-2}, respectively.

4. Conclusions

Carbon deposition by electrolytic heating was undertaken with a tungsten cathode in a water–ethanol solution. Heating was carried out for 30 min under atmospheric pressure. The specimens were examined by optical microscopy, scanning electron microscopy, X-ray diffraction, electron probe microanalysis and Raman spectroscopy. The results were as follows.

(1) No carbon deposition occurred on the wire at voltages lower than 400–500 V with 15–50 mol % ethanol or in less than 10 mol % ethanol. The surface was either irregular with spikes of tungsten or relatively smooth.

(2) Deposition of black bulky carbon occurred on the wire at 550–650 V with 30–50 mol % ethanol.

(3) Disordered graphitic carbon was deposited on the wire when treated at 1240 V for 30 min with 100% ethanol. Applied voltage of 900 V for 18 min yielded glassy carbon with 40 mol % ethanol.

(4) Bulky carbon was obtained on the plate at higher applied voltages with 60–100 mol % ethanol.

(5) Carburization of the tungsten plate to WC and W_2C occurred. The carburization to WC increased with increasing the voltage and the ethanol concentration.

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