Assessment of Electrodes Prepared from Wafers of Boron-doped Diamond for the Electrochemical Oxidation of Waste Lubricants

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ABSTRACT

Electrochemical oxidation using boron-doped diamond electrodes is being investigated as a treatment process for radioactively contaminated oily wastes. Previously, it was shown that electrodes coated with a thin film of diamond were able to oxidise a cutting oil but not a mineral oil. These tests were inconclusive, because the electrodes lost their diamond coating during operation. Accordingly, an electrode prepared from a "solid" wafer of boron-doped diamond is being investigated to determine whether it will oxidise mineral oils. The electrode has been tested with sucrose, a cutting oil and an emulsified mineral oil. Before and after each test, the state of the electrode was assessed by cyclic voltammetry with the ferro/ferricyanide redox couple. Analysis of the cyclic voltammogram suggested that material accumulated on the surface of the electrode during the tests. The magnitude of the effect was in the order:- emulsified mineral oil > cutting oil > sucrose. Despite this, the results indicated that the electrode was capable of oxidising the emulsified mineral oil. Confirmatory tests were undertaken in the presence of alkali to trap the carbon dioxide, but they had to be abandoned when the adhesive holding the diamond in the electrode was attacked by the alkali. Etching of the diamond wafer was also observed at the end of the tests. Surface corrosion is now regarded as an intrinsic part of the electrochemical oxidation on diamond, and it is expected that the rate of attack will determine the service life of the electrodes.

INTRODUCTION

AWE (formerly known as the Atomic Weapons Establishment) is investigating options for the disposal of radioactively contaminated oily wastes and residues. At present, oils containing very low levels of radioactivity can be disposed of by incineration at an off-site location. Also small volumes of oil containing low levels of radioactivity can be encapsulated in cement for disposal to the UK's national repository at Drigg in Cumbria. However, as yet, there is no suitable technology to treat those oils equivalent to Intermediate Level Waste (ILW) or to treat larger volumes of Low Level Waste (LLW) oils.

Electrochemical oxidation using boron-doped diamond electrodes is a possible treatment process for LLW or ILW oils. Potentially, it could be used to oxidise the oils to carbon dioxide, which would facilitate the disposal or recovery of the radioactive material. Oxidation on diamond would have the further advantage in that it would use environmentally benign chemicals.

AWE has examined the oxidation of various non-radioactive oils using an electrochemical cell equipped with electrodes coated with boron-doped diamond (1, 2). These electrodes were found to lose their diamond coating during operation. This did not appreciably affect their ability to oxidise either sucrose or a cutting oil (Solcut BR), but the electrodes were unable to oxidise mineral oil, even when the oil was emulsified using surfactants. The loss of the diamond coating hindered the interpretation of the test results. It was not possible to determine whether the lack of oxidation of the mineral oil was due to the loss of the coating or to some more fundamental chemical limitation of boron-doped diamond.

Electrodes manufactured from "solid" wafers of boron-doped diamond have recently been placed on the market. Although they are only available on the laboratory scale, it was expected that these electrodes would be more robust than the coated electrodes and that they would provide the opportunity to determine whether, in principle, diamond electrodes are capable of oxidising mineral oils. This paper presents work using a 3 cm^2 wafer of boron-doped diamond that has enhanced AWE's understanding of the nature of the oxidation.

EQUIPMENT, MATERIALS AND METHODS

Previous studies (1, 2) had used diamond-coated electrodes with a nominal electrode area of 1000 cm^2 that were supplied by Condias, Fraunhofer Strasse, Itzehoe, Germany. These electrodes had been manufactured by chemical vapour deposition onto a niobium substrate from methane as the source of the carbon for the diamond, and diborane as the source of the boron.

The present study used a DIAFILM PE ™ electrode supplied by Windsor Scientific Ltd., 264 Argyll Avenue, Slough Trading Estate, Slough, Berkshire, SL1 4HE, England. The electrode incorporated boron-doped diamond manufactured by Element 6 (part of DeBeers). This diamond was also manufactured using CVD but it was produced in the form of a wafer, 2 cm diameter and approximately 0.5 mm thick. The wafer had been placed on a tungsten support and mounted in a plastic body using an epoxy adhesive. (Fig. 1, photograph a). Traces of the epoxy adhesive are apparent as dark patches in Fig. 1, photograph b.

This electrode was incorporated into an electrochemical cell using a narrow form 250 ml beaker (Fig. 1, photograph c). The counter electrode was a stainless steel spatula (Fisher Scientific) and the cell was equipped with a silver/silver chloride reference electrode. The electrical potential was provided by an Autolab PGStat30 Potentiostat / Galvanostat (EcoChemie B.V., Utrecht, The Netherlands) with PC control through proprietary General Purpose Electrochemical System software, as supplied by Windsor Scientific Ltd. (Fig. 1, photograph d). A dummy test cell was used to periodically check the operation of the Autolab potentiostat.

Cyclic Voltammetry
The response of the cell was characterised by cyclic voltammetry using the ferro/ferricyanide redox couple. The electrolyte contained 1 mM potassium ferricyanide and 1 mM potassium ferrocyanide in 0.1 M potassium chloride. The electrolyte was not stirred and the tests were performed at ambient temperature (generally 20 – 25 ^oC). The diamond electrode was set as the working electrode and the steel electrode was the counter electrode. Cyclic voltammetry was performed according to the "normal" profile in the General Purpose Electrochemical System

software. The potential of the diamond electrode was cycled between – 1 and + 1 volt against the silver/silver chloride reference electrode. The scan rate was 0.1 volt/second and the step potential was 0.01 V. The profile of current vs. potential was recorded after 5 cycles.
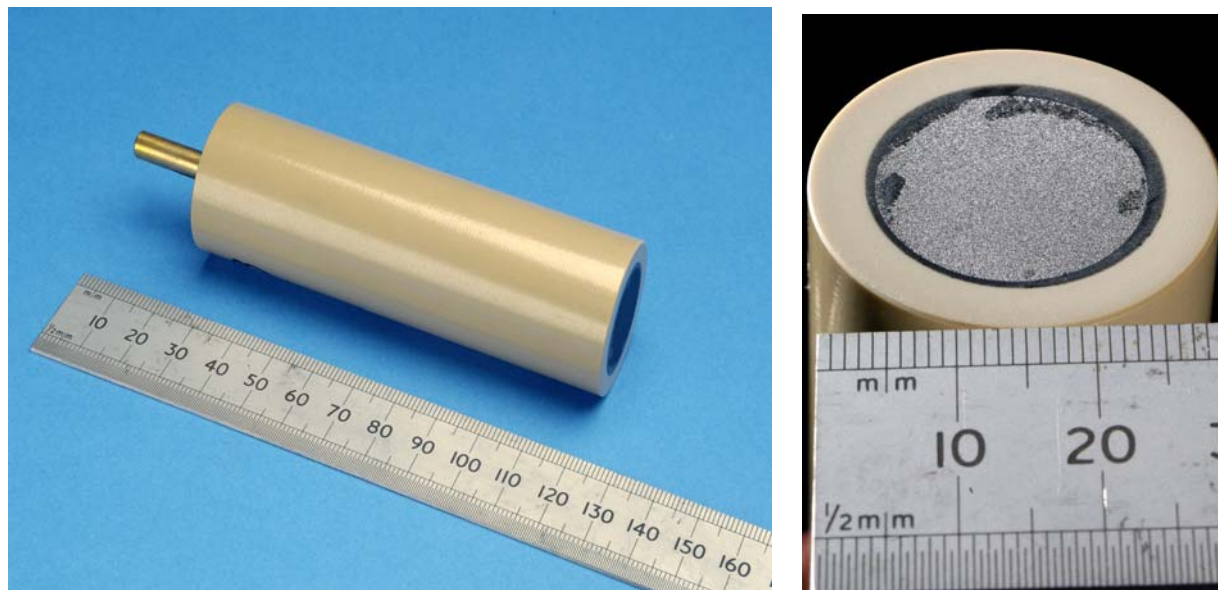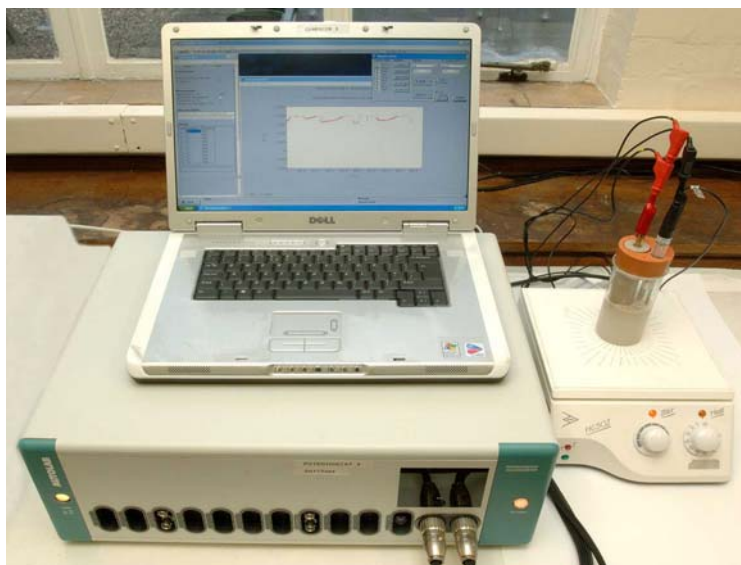

(a)

(b)
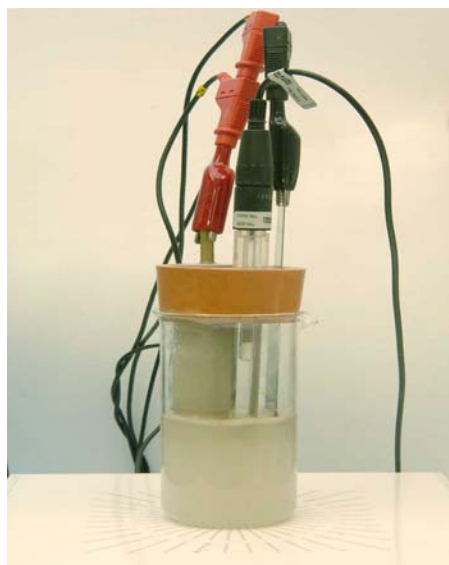
(c)

(d)

Fig.1. Electrode incorporating a wafer of boron-doped diamond assembled in an electrochemical cell

Electro-oxidation
Electrochemical oxidation was performed in a stirred electrolyte that contained the test organic compound and 0.031 M sodium sulphate in demineralised water. The current was held at 100 milliAmperes, and the oxidation was run as a batch operation. The temperature of the electrolyte was not controlled, and it generally reached $20 - 30\ ^oC$ (the exact value being determined by the ambient temperature and the potential required to deliver a current of 100 mA).

The sources of the test organic compounds were:

|	
Sucrose	Food grade sugar
Solcut BR	Houghton Vaughan (although this cutting oil is no longer manufactured). Solcut BR was formulated with severely refined mineral oil, petroleum sulphonates, potassium salts of tall oil, oleate ester of polyethylene glycol, xylenol rich cresylic acid and a trace of antifoam).
Tellus R10 oil	Shell
Atlas and Brij surfactants	Uniquema (formerly ICI Surfactants)

The amount of organic material in the electrolyte was monitored via its Chemical Oxygen Demand (COD) and content of Total Organic Carbon (TOC). Samples were taken periodically during the course of each run and analysed using Dr Lange test kits (LCK014, LCK114 and LCK314 for COD; LCK381 and LCK 380 for TOC) and a LASA20 photometer. When alkali was added to the electrolyte to trap the carbon dioxide, samples were neutralised and immediately assayed for Total Inorganic Carbon (TIC) content using the TOC tests kits or the carbonate test kit (LCK 388).

The current efficiency of the oxidation was calculated from the decrease in the COD and the charge passed. The equation for the oxidation of a carbohydrate, such as sucrose, can be expressed as:-

$$2H_2O \rightarrow 2H_2 + 2[O]$$
$$[CH_2O] + 2[O] \rightarrow CO_2 + H_2O$$

The loss of 1 mole of COD requires the transfer of 4 mole of electrons, which is equivalent to a charge passed of 4 Faraday, i.e. 4 x 96479 amp.second = 26.8 amp.hours.

It was assumed that the cutting oil and mineral oil could be represented by the formula $C_{17}H_{36}$ with oxidation proceeding according to the equation:-

$$C_{17}H_{36} + 52\ [O] \rightarrow 17\ CO_2 + 18\ H_2O$$
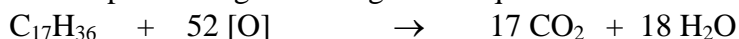
However, this equation over-estimates the amount of oxygen (i.e. electrical charge) needed for the complete oxidation of Solcut BR, because the cutting fluid is a complex mixture of organic chemicals that includes fatty acids and other compounds containing oxygen.

RESULTS AND DISCUSSION

Electrochemical oxidation mediated by boron-doped diamond anodes is thought to involve the generation of hydroxyl radicals, which react with the organic material either on or very close to

the electrode surface (3, 4). Consequently, the previous findings (1, 2) that the diamond-coated electrodes were able to oxidise a cutting oil but not an emulsified oil may be linked to the nature of the diamond surface. It has been shown that the application of different pre-treatments to diamond electrodes produces different oxidative/reductive responses during cyclic voltammetry (5, 6). It was considered that this technique might yield an insight into the behaviour of the electrode used in the present study.

The same organic substrates (i.e. sucrose, Solcut BR cutting fluid and emulsified Tellus R10 mineral oil) that had been used with the coated electrodes were tested with the wafer of boron-doped diamond. The state of the diamond electrode was assessed before and after each of the sequential oxidation tests by cyclic voltammetry.

Characterisation by Cyclic Voltammetry

Before the electrochemical cell was used for oxidation, it was characterised by cyclic voltammetry using the ferro/ferricyanide couple (Fig. 2).
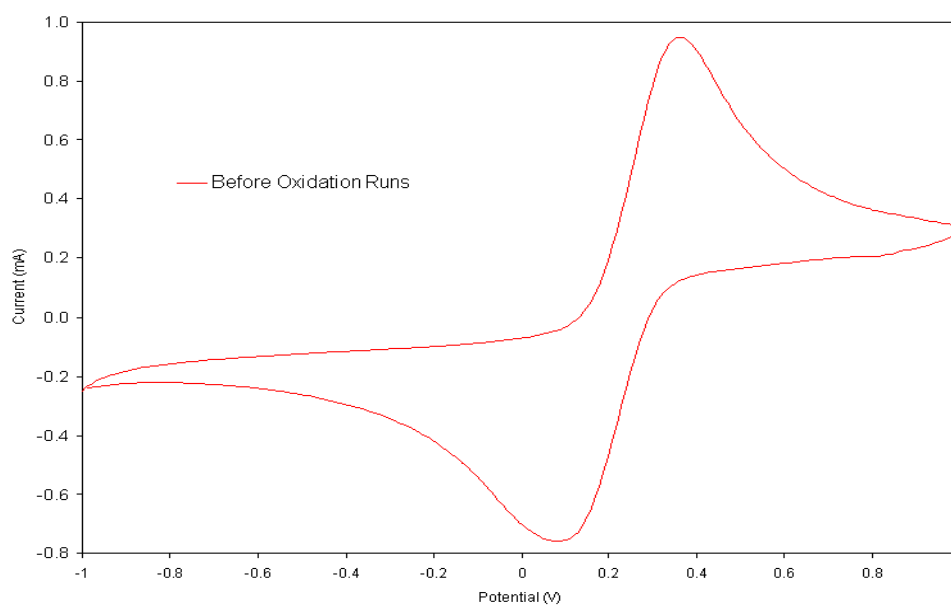

Fig. 2. Cyclic voltammetry with ferro/ferricyanide before oxidation runs

The measured scan of current vs. potential was similar to that given in the literature (5). The upper part of the curve shows the current as the potential was increased from – 1 V to + 1 V. The sharp increase in the current occurred at the potential at which ferrous ions were oxidised to ferric (7). Because the solution was not stirred, the concentration of ferrous ions close to the

diamond electrode was rapidly depleted, so leading to a fall in the current as the potential increased to $+$ 1 V. The lower curve represents the analogous situation with the reduction of ferric to ferrous when the potential was decreased from $+$ 1 V to $-$ 1 V. The peak in the current corresponding to the oxidation of Fe^{II} occurred at 0.36 V and the peak corresponding to the reduction of Fe^{III} occurred at 0.1 V.

Oxidation of Sucrose

The oxidation run with sucrose served to commission the electrochemical cell. Electro-oxidation started with a concentration of 8 g sucrose per litre and a current of 100 mA. It was found that a cell potential of about 6 - 6.5 V was required to maintain this current. The diamond wafer permitted an effective oxidation of sucrose, as shown by the reduction of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) (Table I).

Table I. Oxidation of Sucrose

	Run Time (hours)			
	18	26	41	48
Overall reduction of TOC (%) [a]	35	57	96.6	99.6
Overall reduction of COD (%) [a]	49	70	97.4	99.8
Time Interval (hours)	0 - 18	18 - 26	26 - 41	41 - 48
Current Efficiency (%) of Time Interval	119	108	75	13

[a] Measured initial TOC = 3.52 g/l, COD = 9.08 g/l

Initially, the reduction of the TOC lagged behind the reduction of the COD. This was observed previously with the diamond-coated electrodes (1), and it was ascribed to the formation of oxygenated intermediates rather than carbon dioxide in the early stages of the run. The current efficiency was high initially, and it did not fall until over 50% of the sucrose had been oxidised. This confirmed that the apparatus was functioning as expected.

At the end of the run the electrode was subjected to cyclic voltammetry after being rinsed in demineralised water. The shape of the plot of current vs. potential was somewhat different to that recorded before the run (Fig. 3). The current at both extremes of the potential range was higher and the difference in current between the upper and lower scans was greater than before the run. This behaviour is generally taken to indicate the presence of contaminants on the surface of the electrode. The peaks in the current were somewhat closer together, i.e. they occurred at 0.32 V and 0.13 V, which indicated that the electrode was still able to efficiently oxidise and reduce the ferro/ferricyanide couple.
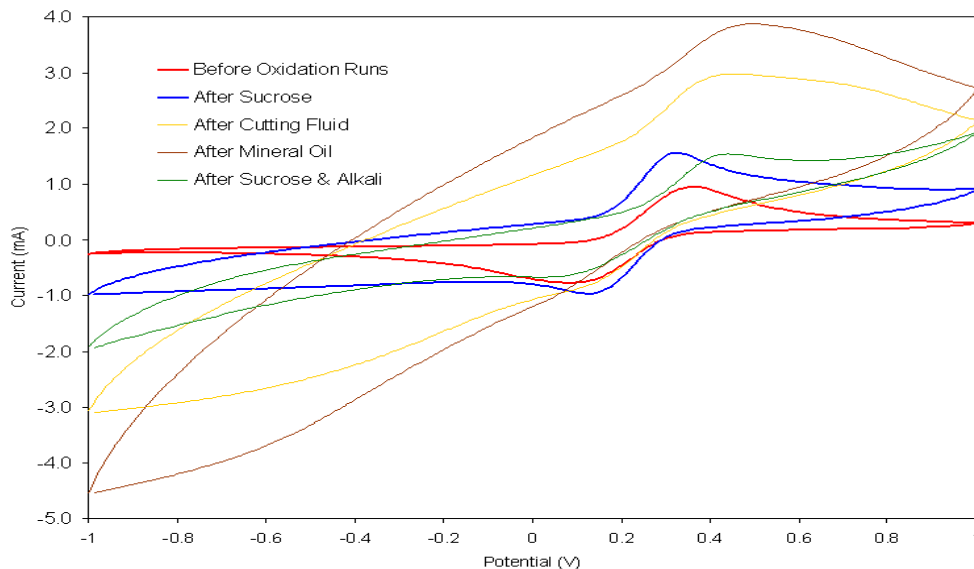
Fig. 3. Cyclic voltammetry with ferro/ferricyanide after oxidation runs - subsequent scans
superimposed on the initial scan
(Note the change of scale of the current axis compared to Fig. 2)

Oxidation of Solcut BR Cutting Fluid

The diamond-wafer electrode was then tested with Solcut BR, again starting with 8 g/l of the
organic material. The applied current was maintained at 100 mA, but this required a higher cell
potential than with sucrose. Moreover, the cell potential varied rapidly between about 6.4 and
8.0 V. Despite this anomaly, the diamond wafer was able to oxidise Solcut BR (Table II). The
time required for oxidation was longer than in the first run because Solcut BR has a greater TOC
and COD than sucrose (on a weight for weight basis).

Table II. Oxidation of Solcut BR

	Run Time (hours)			
	24	48	95	160
Overall reduction of TOC (%) [a]	32	52	85	96.1
Overall reduction of COD (%) [a]	37	58	85	96.2
Time interval (hours)	0 – 24	24 - 48	48 – 95	95 – 160
Estimated Current Efficiency (%) over time interval shown above	151	85	52	15

[a] Measured initial TOC = 5.26 g/l, COD = 20.4 g/l

The estimated current efficiency was greater than 100% over the initial stages. Possible
explanations for this are:- errors in sampling and measuring the TOC/COD of the oily emulsions
or atmospheric oxygen took part in the reaction.

When the cyclic voltammetry was repeated after the oxidation run (Fig. 3), a major change in the shape of the plot of current vs. potential was observed. The current at the extremes of the potential range was higher than in the previous scans. This swamped the reductive peak. The peak in the oxidative current was broader and it occurred at a higher potential than before the run, i.e. at 0.4 V compared to 0.32 V. The change in the shape of the scan probably indicates that the amount of contaminant material on the electrode had increased during the run, even though an appreciable proportion of the Solcut BR had been oxidised.

Oxidation of Mineral Oils

After confirming that the electrodes could oxidise Solcut BR, work moved on to the next stage, which was to examine the oxidation of the mineral oil, Tellus R10. The oil was emulsified in a 1:1 mixture of Atlas G1096 and Brij 92V surfactants. When the emulsion was treated under the same conditions, it was found that the cell potential required to maintain 100mA was even higher than that with the cutting fluid. Furthermore, the fluctuations were even greater (about 6.7 - 13 V compared to 6.4 – 8.0 V with Solcut BR).

There was an apparent rapid oxidation of the emulsified mineral oil during the run (Table III).

Table III. Oxidation of Emulsified Mineral Oil

	Run Time (hours)		
	46	94	163
Overall reduction of TOC (%) [a]	90	93	92
Overall reduction of COD (%) [a]	89	93	87
Time Interval (hours)	0 - 46	46 - 94	94 - 163
Current Efficiency (%) of Time Interval	209	~10	-

[a] Measured initial TOC = 4.88 g/l, COD = 22.3 g/l

However, the reduction of the TOC and COD over the first 46 hours was much greater than expected from theoretical consideration. This may have been due to sampling errors. Some oil separated from the emulsion during the oxidation run, and so the samples may not have been representative of the bulk electrolyte.

Cyclic voltammetry revealed that the changes in the state of the electrode that were observed at the end of the previous run with the cutting fluid were more pronounced with the mineral oil (Fig. 3). As before, only the oxidative peak could be detected in the scan. The peak for the oxidative current had shifted at a higher potential of 0.46 V. Presumably, this reflected an even greater accumulation of material on the electrode.

Oxidation under Alkaline Conditions

An attempt was made to confirm the oxidation of the emulsified mineral oil by performing the tests under alkaline conditions in order to trap the liberated carbon dioxide. After a preliminary test with sucrose , which showed that the pH had to be held at $\geq \sim 9$, the methodology was checked by oxidising sucrose in an electrolyte containing 0.6 M sodium hydroxide to provide an excess of alkali throughout the run. The presence of the alkali appeared to impede oxidation to some extent. After 66 hours the measured loss of TOC and COD was 89 % and 95 %

respectively (compared to > 99% without alkali (Table I)). Controls showed that the uptake of carbon dioxide from the atmosphere in this period would have been negligible. The amount of inorganic carbon measured at the end of the run accounted for 74% of the initial organic carbon.

Cyclic voltammetry showed that the 2 runs with sucrose and alkali (i.e. the preliminary test and the run reported here) led to a partial recovery of the ability of the electrode to reduce ferricyanide (Fig. 3). A small reductive peak was observed at 0.017 V. At the same time, the maximum currents at the extremes of the potential range were lower and the oxidative peak had moved to a slightly lower potential (0.44V). This suggested that the material deposited on the electrode during the oxidation of the oils had been partially removed.

These cyclic voltammetry tests were performed before starting the confirmatory test with the emulsified mineral oil. The initial electrolyte contained 0.67 M sodium hydroxide, and more sodium hydroxide equivalent to 0.15 M was added after 93 hours. This test had to be abandoned because the electrode disc became partially detached from the tungsten support plate during the run, presumably, due to the effect of the alkali on the epoxy adhesive holding the diamond disc in place.

Final State of the Electrode Surface

When the used electrode was removed from the cell for inspection, etching of the diamond was apparent as irregular score marks on the surface. (Fig. 4).
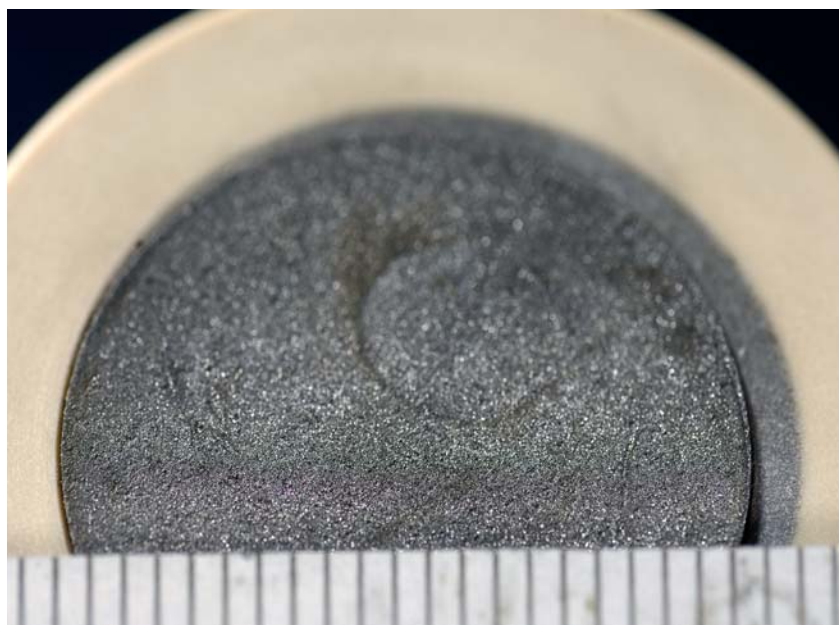

Fig. 4. Appearance of electrode after use

Although boron-doped diamond is mechanically robust, this test shows that it is susceptible to electrochemical attack. It has been reported that the presence of methanol or acetic acid (as model organic compounds) in an electrolyte stimulates the corrosion of the surface of coated electrodes (6). This corrosion may be a consequence of the electrochemical reactions taking part

on the surface. It was proposed that the hydroxyl radicals generated at a diamond electrode initially react with any carbon that is present in the diamond as the graphite (sp^2) form rather than as the diamond (sp^3) form (6). When the hydroxyl radicals have reacted with all the graphite carbon, they react with the carbon on the surface of the diamond crystals. The continual use of diamond for oxidation leads to irreversible changes due to the formation of C-OH or C=O bonds on the surface of the diamond (6). The boundaries between the crystals are thought to be particularly susceptible to attack. Opening up of the grain boundaries then allows attack at the interface between the diamond and the support material.

Surface corrosion is an intrinsic part of the electrochemical oxidation on boron-doped diamond electrodes. This is now openly recognised as a factor that will determine the service life of these electrodes (8). In the present tests with a wafer of boron-doped diamond, the lifetime of the electrode was determined by the poor resistance of the epoxy adhesive to the alkali used in the tests, rather than by the surface corrosion of the wafer. The electrode was subjected to about 66 amp.hours usage (equivalent to about 20 amp.hours per cm^2). A theoretical consideration (based on the equation shown in the Methods section) suggests that the destruction of 1 gram of oil with a nominal formula = $C_{17}H_{36}$ would require 11.6 amp.hours. Assuming that a lifetime of 100 amp.hours per cm^2 (= 10^6 amp.hours per m^2) is achievable, the destruction of 1 tonne of oil (about 1.1 m^3 volume) with 100% current efficiency would require 11.6 m^2 of electrode surface.

CONCLUSIONS

It is becoming apparent that surface corrosion is an intrinsic part of the electrochemical oxidation on boron-doped diamond electrodes. Although surface corrosion will limit the service life of the electrodes, in the present study the lifetime of the electrode incorporating the wafer of boron-doped diamond was determined by the sensitivity of the epoxy adhesive to alkali rather than by the etching of the wafer. The consequence of this unforeseen sensitivity to alkali was that it was not possible to determine whether, in principle, diamond electrodes are capable of oxidising mineral oils. However, the results obtained were sufficiently encouraging that the work is continuing using less aggressive conditions.

It was estimated that the destruction of 1 tonne of oil might require 11.6 m^2 of electrode surface, if a lifetime of 100 amp.hours per cm^2 and 100% current efficiency are achievable. Whether this will be acceptable or not will depend on the cost of the electrodes. At the moment, the technology is in its infancy and mass production / marketing is needed to drive down the cost of producing electrodes with a suitable thickness of diamond.

ACKNOWLEDGEMENTS

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