Dry micro-electro-discharge machining of carbon-nanotube forests using sulphur-hexafluoride

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ABSTRACT

The effect of using sulphur hexafluoride (SF₆), a high-dielectric-strength gas, for dry micro-electro-discharge machining (µEDM) of carbon-nanotube (CNT) forests is investigated. It is found that SF₆ enables µEDM of CNTs without O₂, which is known to be essential for CNT machining in N₂. The process in the SF₆ ambient at a discharge voltage of 25 V is found to lead to a smaller discharge gap, i.e., tighter tolerance as well as higher machining quality compared with the N₂ case at the same voltage. The N₂ environment produces smaller discharge gap when 10 V is used; however, both the quality and rate of machining are somewhat lower in this case. The mixture with 20% O₂ in SF₆ is revealed to be an optimum condition for machining tolerance and quality. CNT forests are used as the cathode in the process, as opposed to conventional µEDM, where the workpiece forms the anode. This configuration in the SF₆–O₂ mixture is observed to generate higher discharge currents at low voltages, presumably due to effective field-emission by the CNTs, leading to finer and cleaner machining. Energy-dispersive X-ray analysis reveals that the optimal conditions result in less contamination by the electrode element on the processed forest surfaces.

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1. Introduction

Carbon nanotubes (CNTs) have highly attractive mechanical, electrical, optical, and thermal properties [1–5]. Densely packed, vertically aligned CNTs, commonly referred to as CNT forests, have many potential uses in different engineering fields as summarised in [6]. Patterning of CNT forests is crucial to make them useful for various applications. Selective growth of the forests by chemical vapour deposition (CVD) on pre-patterned catalyst on the substrate is widely used to produce two-dimensionally patterned CNT forests with uniform height. Recently, a micro-electro-discharge machining (µEDM) based process has been developed to enable three-dimensional, free-form patterning of microstructures in bare CNT forests [7–10]. This process used dry air as the dielectric medium, instead of the dielectric liquid used in typical µEDM, as the forest structures patterned in liquid are drastically modified when the structures are dried because of capillary effects [7]. This technique was further studied to investigate the possible removal mechanism of CNT forests in dry µEDM, suggesting that the process was essentially oxygen plasma etching rather than the conventional, direct thermal removal (evaporation and melting) process, and that air (or N₂ with ~20% O₂) was an optimal medium for µEDM of CNT forests [8,9]. The machining tolerance, or the discharge gap clearance between a forest and the µEDM electrode, was reported to be 10 µm or more, substantially larger than typical values (of one to a few µm) involved in standard µEDM with dielectric liquid. In typical EDM (including µEDM), the workpiece and the electrode are generally arranged to be...
the anode and the cathode, respectively, as this polarity usually results in efficient material removal with small electrode wear. Most of the previous studies on μEDM of CNT forests [7–9], as well as of carbon nanofibers [11], also used this conventional polarity, i.e., the carbon material served as the anode. Because of their extremely small tips with nanometer radii and high aspect ratios, CNTs are known to have excellent electron field-emission properties compared to the tungsten tip (a typical material used as μEDM tool) [12]. It has recently been found that reverse-polarity μEDM of CNT forests that are defined as the cathode in air ambient enhances the patterning tolerances and quality with decreased discharge energies [6]. In addition, all these previous studies have used the mixture of N₂ and O₂ (in the form of air in most cases) as the machining medium, and the effect of other gases on the μEDM performance has not been investigated so far. Sulphur hexafluoride (SF₆) has a dielectric strength much higher than that of N₂ [by a factor of ~3] [13]. This suggests that in SF₆, the machining electrode and the workpiece (CNT forest) have to come closer in order to cause a gas breakdown for a given electric field strength. Hence, the use of SF₆ may further reduce the discharge gap in the μEDM process compared to the case with N₂ under the same discharge voltage.

The present work investigates μEDM of pure CNT forests using a new gas, SF₆. In the previous studies, it was reported that O₂ was necessary for successful μEDM of CNT forest in a N₂ environment [8,9]. This is unknown for an SF₆ environment, which is experimentally investigated as part of this work. The study also explores the effect of O₂ mixed in SF₆ on the CNT removal process, and its comparison with the conventional N₂–O₂ environment. The characteristics of normal- and reverse-polarity μEDM for CNT forests in the SF₆–O₂ gas system and the patterned structures are studied to reveal various advantages over the conventional process in air ambient.

2. Sample preparation and experimental set-up

The CNT forest samples used in this study were grown on highly doped silicon substrates ((100) n-type, resistivity 0.008–0.015 Ω cm) using an ethylene-based atmospheric-pressure CVD system and iron catalyst. Details of the growth condition and system used for the sample preparation can be found in [6]. The process yielded forests of vertically aligned multi-walled CNTs with heights of up to several 100’s of μm on 5-mm² surface areas.

The experiments for μEDM of the CNT forests were performed using a servo-controlled 3-axis μEDM system (EM203, SmalTec International, IL, USA) with a 0.1-μm positioning resolution. The discharge pulses were generated with a relaxation-type resistor–capacitor circuit [14], a proven pulse generator used for μEDM of CNTs [7–9]. The machine is capable of detecting undesired short-circuit events during operation and can retrieve the electrode held on the Z-axis stage upward to overcome a short circuit; once the short circuit is cleared, the electrode feeding is automatically resumed. The experimental set-up arranged for the machining tests and characterization is illustrated in Fig. 1. As shown, a current probe (CT-1, Tektronix, OR, USA) was used to monitor pulses of the discharge current in real time. The discharge current data were captured from the oscilloscope using a GPIB interface and stored in a computer for subsequent analysis. Further, O₂ was first mixed with either SF₆ or N₂ inside a buffer chamber, and the mixed gas was introduced to the machining chamber, where the O₂ concentration was measured using an oxygen sensor (VN202, Vandagraph Co., UK). The flow rates of O₂ and SF₆/N₂ were adjusted so that the O₂ concentration reached the target value and was stabilized in the machining chamber for at least 5 min prior to machining. In this study, a series of μEDM experiments at both the normal and reverse polarities were performed using cylindrical tungsten electrodes rotating at 3000 rpm. The μEDM conditions are summarized in Table 1. A 10-pF capacitor was used in the discharge circuit for all the experiments in this study.

3. Results and discussion

As mentioned earlier, in air, μEDM of CNT forests with the reverse polarity using the forests as the cathode was demonstrated to result in higher performance than the normal-polarity case [6]. In this configuration, effective removal at very low voltages (~10 V) was achieved due to higher currents of the discharge pulses apparently because of the field-
emission properties of the CNT cathode. To evaluate the effect of the SF$_6$ environment for reverse EDM of CNT forests, machining tests with both the normal and reverse polarities were first conducted in a gas mixture of 50% SF$_6$ and 50% O$_2$. A 64-µm-diameter electrode was scanned along a square path of 200 µm by 200 µm in a CNT forest while machining it at 25 V to a depth of 25 µm. Fig. 2 shows the structures machined at both polarities, as well as the electrode used for each case imaged after the process without cleaning. It is clear from Fig. 2a and b that the reverse-polarity process resulted in finer and sharper structures compared with the normal-polarity case, the latter exhibiting distorted shapes and rough surfaces in the machined structures. In this EDM condition at 25 V, the reverse-polarity process was observed to generate relatively high discharge current (~16.3 mA) that is evidently sufficient to induce desirable material removal governed by electrical discharges. In the case of the normal polarity, however, the discharge current was much lower (~5 mA), leading to insufficient removal by electrical discharges, therefore causing mechanical abrasion and distorted structures/surfaces. These tendencies in terms of the discharge current and machining quality are consistent with the results obtained in air [6].

As also can be seen in Fig. 2, reverse-polarity µEDM resulted in much cleaner (less debris) structures, whereas the normal-polarity case produced more debris left on the structures and the debris accumulated on and stuck to the electrode. The debris accumulation on the electrode increases its effective diameter in a random and non-uniform manner, leading to an undesired larger gap between the walls of the resultant structures (as shown in Fig. 2a and b), thus lowering the precision in the machining process. A possible explanation for the above result may be similar to the case with reverse µEDM in air [6] – with reverse polarity, the CNT forest is the cathode and thus not subject to electron bombardment (which induces conventional thermal removal as noted earlier) in principle; therefore, CNT removal is expected to be almost entirely due to oxygen and/or fluorine plasma etching [9,15,16] that decomposes CNTs into volatile products, forming minimal debris. With the normal-polarity condition, in contrast, the forest is the anode that is bombarded by electrons during the process and may be subject to some level of thermal removal where parts of the CNTs are melted and blown by pressure waves induced by the intense heat that the pulsed discharge produces, leaving resolidified carbon debris on the workzone and on the electrode. Based on the comparison above, the subsequent experimentations in the present study were carried out in the reverse-polarity mode, which provides more desirable results in machining precision and quality.

In order to evaluate the effect of SF$_6$, in comparison with the conventional N$_2$, used as the dielectric gas on reverse µEDM of CNT forests, machining tests were performed with 100% SF$_6$ ambient as well as with 100% N$_2$ ambient. Two basic discharge phenomena in EDM should be noted before the results of the above experiment are discussed. Gas discharges can be classified into several categories based on the corresponding voltage and current values. In EDM, there are two types of discharges that most commonly occur, namely spark and arc. Spark is characterised with higher discharge voltages compared to arc. Furthermore, spark is a transient process which may ultimately lead to a continuous arc if certain electrical conditions are fulfilled. In EDM, including µEDM, it is

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values used</th>
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<tbody>
<tr>
<td>Machining voltage (V)</td>
<td>25 or 10</td>
</tr>
<tr>
<td>Capacitance (pF)</td>
<td>10</td>
</tr>
<tr>
<td>Electrode feed rate during EDM (mm/min)</td>
<td>Z: 0.03, X-Y: 1</td>
</tr>
<tr>
<td>Ambient</td>
<td>O$_2$% in SF$_6$ (for the SF$_6$–O$_2$ system) 50, 20, 10, or 0</td>
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<tr>
<td></td>
<td>O$_2$% in N$_2$ (for the N$_2$–O$_2$ system) 20 or 0</td>
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Fig. 2 – Scanning electron microscope (SEM) images of the microstructures machined in a CNT forest in 50% SF$_6$ and 50% O$_2$ at 25 V with (a) the normal polarity and (b) the reverse polarity. Optical images of the tungsten electrode after machining with (c) the normal polarity and (d) the reverse polarity.
desired to have spark discharge rather than arcing, which is detrimental as it results in excessive heating that causes severe damage to the sample surfaces [17]. Fig. 3a and b shows typical discharge currents measured with 100% N₂ and 100% SF₆, respectively. As represented in Fig. 3b, the 100% SF₆ case produced short pulses (pulse duration ~10 ns), indicating a spark-mode discharge. These pulses usually had a peak current of around 10 mA or less but also showed spontaneous very large peak currents (30–40 mA) occasionally. For the 100% N₂ case (Fig. 3a), the process tended to produce longer pulse durations that led to frequent abnormal arcing. (These two different discharge modes, spark and arc, were also distinguishable visually through the on-machine microscope; the former case was typically observed to emit white light whereas the latter mode was with yellow-orange light emissions.) Moreover, arcing resulted in frequent short-circuit detections, preventing proper machining. Fig. 4a and b compare the results obtained in 100% N₂ and 100% SF₆, respectively, to produce the same square patterns as those in Fig. 2a and b. Fig. 4a exhibits damage on the forest surface and the sidewall of the resultant structure is smoother (free from extended layers) for SF₆ ambient. Possible sources of phenomena may occur with plasmas in the form of spark discharge, which could be the case shown in Fig. 4b. The possible reason of frequent arcing in 100% N₂ can be understood from the fact that N₂ is less electrically resistive than SF₆ and thus permits the discharge gap to sustain a continuous arc between the electrode and the forest surface [13,18,19].

As noted earlier, the presence of O₂ in the μEDM process was reported to be essential for proper removal of CNTs in N₂ ambient, in which the optimal concentration of O₂ was ~20% [8,9]. To study the role of O₂ in the SF₆ case, the μEDM process was characterised with O₂ concentrations of 10%, 20%, and 50%. The results machined at 25 V shown in Fig. 5 suggest that the structural and surface quality improved with increasing O₂ concentration up to 20% (Fig. 5a and b), and that the structures became distorted (e.g., the top surface of the centre post as seen in Fig. 5c, possibly due to sparks propagating and etching portions of it) again when the concentration was further increased to 50%. The structure machined at 10 V and 20% O₂ in SF₆ shown in Fig. 5d indicates deteriorated structural quality compared to Fig. 5b, the 25-V case under the same ambient. The results obtained at the same voltage levels, 25 V and 10 V, with 20% O₂ in N₂ ambient are shown in Fig. 5e and f, respectively. These suggest that, in contrast to the SF₆–O₂ ambient cases, the 10-V condition led to higher machining quality than the 25-V condition in the N₂–O₂ ambient; this result is consistent with the previous findings reported in [6]. However, a comparison between Fig. 5b and f, representing the conditions that provided the highest machining quality for the SF₆ and N₂ environments, respectively, suggests that SF₆ results in sharper corners (without extended portions at the corner of the centre post) than N₂, and the sidewall of the resultant structure is smoother (free from extended layers) for SF₆ ambient. Possible sources of the different optimal voltage levels for the SF₆ and N₂ environments (25 and 10 V, respectively) found above will be discussed later.

Fig. 6a shows the measured values of the average peak discharge current (calculated from 300 individual discharge pulses) and of the discharge gap as a function of O₂ concentration in SF₆. The discharge gap was calculated as the half of the dimensional difference between the measured width of a groove machined in a forest and the diameter of the electrode used. Fig. 6b compares the discharge gaps measured in the structures obtained with the SF₆ and N₂ environments (both at 20% O₂) at the two discharge voltages of 25 and 10 V. Fig. 7 shows the measured Z position of the electrode captured during machining processes with different gas compositions and discharge voltages. The ripples seen in Fig. 7 were caused by the retraction motion of the Z stage due to the short-circuit events occurred in the processes as noted earlier. As shown in Fig. 6a, the discharge current was observed to have an increasing trend with O₂ concentration in SF₆ at 25 V; however, the discharge gap exhibited the minimal value (of 4.2 μm) at 20% O₂. These results may be explained as follows: The O₂ concentration at 10% caused frequent short-circuit detections as shown in Fig. 7, which provided more energy for plasma etching noted earlier, resulting in a larger gap. For the 100% SF₆ (O₂ free) case, although the machining was observed to be smooth (with little short-circuit detection as shown in Fig. 7) with a low average peak current (~5 mA),
the very large pulses (with peaks of 30–40 mA) occasionally observed in this 100% SF₆ condition discussed earlier may have caused larger removal and discharge gap. For an O₂ concentration above 20%, the process generated short pulses
with higher peak currents in a consistent manner, which also led to a larger discharge gap.

As discussed above and shown in Fig. 6b, in SF\textsubscript{6} (at 20% O\textsubscript{2}), processing at 25 V resulted in the minimum discharge gap and the highest machining quality; however, 10 V may have made the discharge gap too small because of the high-dielectric ambient and thus caused physical touching and mechanical rubbing between the rotating electrode and the forest surface (which may have caused the circular marks on the bottom of the structure shown in Fig. 5d) due to non-ideal mechanical/positioning instability in the \( \mu \)EDM system used, deteriorating the processed structure/surfaces. This undesired mechanical contact may have also occurred on the sidewalls of the patterned structures and caused slight bending or displacement of the CNTs on the walls, which may be the probable cause of the larger gap compared with the N\textsubscript{2} environment case at 10 V (Fig. 6b) and of the very frequent short circuits or long machining time (Fig. 7). In the N\textsubscript{2} environment, on the contrary, the tendency of uncontrolled large spark and/or arcing (similar to the 100% N\textsubscript{2} case) was evident when 25 V was used. This is believed to be a major source of the structural distortion observed (Fig. 5e) as well as the enlarged gap (Fig. 6b). Lowering the voltage to 10 V improved the removal quality (Fig. 5f) while decreasing the discharge gap. However, these favourable features at 10 V in the N\textsubscript{2} case come with the price of machining stability and efficiency – a relatively high rate of short circuiting, presumably due to the low discharge energy causing insufficient removal, was observed to slow the process at this 10-V condition (e.g., Fig. 7 shows that the removal at 10 V in N\textsubscript{2} was \( \approx 1.7 \) times slower than the case at 25 V in the SF\textsubscript{6} environment). This high rate of short circuiting may have also introduced the undulations of the sidewalls of the resultant structure as shown in Fig. 5f.

The elements on the surfaces of the forest microstructures (the bottom of the trenches) reverse-\( \mu \)EDMed in the SF\textsubscript{6}–O\textsubscript{2} ambient were characterised using energy-dispersive X-ray spectroscopy (EDX) at 20-keV beam voltage (the beam spot size was \( \approx 2 \) \( \mu \)m, almost 40\times smaller than the width of the trenches, which ensured that the EDX data were obtained from the bottom of the trenches). The results from the surfaces processed with 20% and 10% O\textsubscript{2} (Fig. 8) indicate insignificant detectable sulphur and fluorine in both cases, suggesting that the use of SF\textsubscript{6} does not cause any considerable contamination caused by the ambient gas itself. A low level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourable characteristic that the process at the optimal O\textsubscript{2} concentration provides. Interestingly, it can be seen that the level of silicon detected is most likely due to the presence of the silicon substrate below the forest. The results also show that the level of tungsten, the contaminant due to wear of the electrode, is much lower at 20% O\textsubscript{2} than the 10% O\textsubscript{2} case, a favourabl...
mains on the substrate surface that is too far from the probed forest surfaces to be detected, given its small amount (as can be seen, even silicon shows up with very small signals, although the substrate is bulk silicon). The other is that iron may be originally present on the forest surface (due to potential tip growth of CNTs) but removed by the EDM process. As regards the tungsten level in the N₂–O₂ environment, a previous report shows 1.25% of tungsten contamination under the condition corresponding to the optimal N₂ case [20]. The tungsten level observed in the current study for SF₆ (2.2%, Fig. 8a) is somewhat larger than the above level; it should be noted, however, that the electrode's (tungsten's) consumption condition can be affected by not only the gas medium but also the electrical contact (contact resistance) to the forest, which can vary from sample to sample, and may lead to variations in the level of tungsten.

4. Conclusions

The effect of using SF₆, a high dielectric-strength gaseous medium, mixed with O₂, a chemical decomposition agent, in dry μEDM of pure CNT forests has been investigated. The characterization was performed for both normal and reverse polarities in the μEDM process. The reverse-polarity condition was found to increase the discharge current, possibly because of superior field-emission properties of CNTs that served as the cathode in the reverse condition. It was found that, in contrast to EDM in N₂, the process could be performed in SF₆ only, without the need for O₂, while the addition of O₂ in SF₆ improved the machining precision/quality. It was demonstrated that reverse μEDM in the new gas system was effective in lowering the machining voltage, leading to finer and cleaner CNT removal compared to the normal-polarity condition. Moreover, with a discharge voltage of 25 V and an O₂ concentration of 20%, the use of SF₆ was revealed to give better results compared to N₂, the conventional ambient medium; the discharge gap could be reduced to 4.2 μm. At a lower voltage level (10 V), an N₂ ambient with 20% O₂ produced an even smaller discharge gap, although the occurrence of short circuits slowed the removal process somewhat. The SF₆–O₂ gas system at 25 V was demonstrated to enable not only more stable and faster processing but also relatively higher machining quality compared to the optimal N₂–O₂ ambient case at 10 V. EDX analysis revealed that reverse μEDM in the optimal SF₆–O₂ ambient leaves more than 90% carbon in the etched region with a minimal amount of the electrode element or the gaseous elements.

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