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Abstract

Carbon nanotubes (CNTs) coated on the WC/Co micropunch, with diameter of 150 μm, for prolonging the life of micropunch were investigated. Carbon nanotubes were synthesized by homemade method. Through scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the morphology and structure of CNTs were expressed. After the punching test, wherein Ti was used as substrate, the effect of CNTs in prolonging the life of micropunch on the wear loss and the surface morphology of micropunch had been studied through confocal laser, SEM, digital balance, etc. Results show that the wear of CNT-coated micropunch obviously decreased; and that even in the severe wear period, the wear loss is lesser than that of non-CNT-coated micropunch. Compared with the micropunch without CNTs coating, the promising results are due to the formation of a transfer film at the contact region by rubbing of the CNT forest. CNTs produced adhered to the micropunch surface, thereby avoiding direct contact during the punching period and providing lubricant properties to the interface due to their graphitic nature. Moreover, the relevant mechanism was primarily illustrated by movable cellular automaton.

Keywords: Carbon nanotubes, Micropunch, Wear characteristic, WC/Co
1. Introduction

Carbon nanotubes (CNTs) [1, 2] are unique nanosystems with extraordinary mechanical and electronic properties due to their unusual molecular structure. CNTs with wall thickness of one carbon sheet are named as single-walled carbon nanotubes (SWCNTs). SWCNTs can be considered as the building blocks of multi-walled carbon nanotubes (MWCNTs), which consist of a coaxial array of SWCNTs with increasing diameter that is from two to several tens of nanometers, thus providing very high aspect ratio structures [2].

In the last decade, an enormous amount of work has been devoted to reveal the unique, structural, electrical, mechanical, and chemical properties of carbon nanotubes and to explore what might be their most interesting applications [3-10]. CNTs showing unique properties, such as high tensile and flexural strengths, high elastic modulus, and high aspect ratio, have also been considered as attractive contenders for tribological applications. In this sense, interesting results have been reported with significant improvements in friction and wear rates for nanotubes-polymers [11, 12], ceramics [13, 14], and metal composites [15, 16]. According to theoretical considerations [17, 18, 19], friction coefficients between the walls of multi-walled carbon nanotubes should be extremely low.

Due to wear of the WC/Co micropunch, the quality of the punched holes significantly deteriorates after about 1,000 punching shots [20]. Furthermore, the cost of the punches is high; therefore, it is desirable to prolong the life of the micropunches.

As mentioned above, CNTs are high in strength and low in friction coefficient. CNTs coated on the surface of micropunches may greatly prolong the tool life by reducing wear loss during punching and by enhancing the wear resistance of the punches.

Consequently, to prolong the life of serving tools in microfabrication, the effects of CNTs coated on WC/Co micropunches on wear resistance improvement were investigated in this research. In the long run, this research can lead to the improvement of wear resistance properties of such tools made of WC/Co and other engineering materials.

2. Experimental material and procedures

2.1. Experimental material

Micropunch (made by Ultrahardness tools company, Japan) with 75% volume fraction WC particle and 25% volume fraction Co particle of 50 μm mean size, 150 μm in diameter was delivered with precisely grinding by experimental requirements. Figure 1 shows the surface texture of micropunch for CNTs coating. Pure titanium sheet with 200 μm in thickness was used as the substrate. Alcohol with a normal purity of 95% was purchased from Sigma Aldrich.
2.2. Experimental procedures

2.2.1. CNTs synthesis

The micropunches were cleaned using acetone and pure ethyl alcohol to remove any possible contaminant and were carefully put into the vacuum chamber prior coating.

For CNTs coating on micropunch, first of all, the catalyst (Fe) was deposited on the micropunch working section by electron cyclotron resonance (ECR) (made by Elionix, Japan), and the related processing parameters are listed in Table 1. At the same time, remains of the micropunch were covered with Al foil to avoid the effect of Co distributed in micropunch because pure Ni, Co, or Fe, and their alloys or compounds are widely acceptable catalysts for the growth of CNTs [21-22].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>WC/Co micropunch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Fe</td>
</tr>
<tr>
<td>Irradiation time</td>
<td>60 s</td>
</tr>
<tr>
<td>Accelerated voltage</td>
<td>2,500 V</td>
</tr>
<tr>
<td>Ion current density</td>
<td>12.0 mA/cm²</td>
</tr>
<tr>
<td>Gas</td>
<td>Ar</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>0.6 SCCM</td>
</tr>
<tr>
<td>Vacuum</td>
<td>1.5×10⁴ Pa</td>
</tr>
</tbody>
</table>

Table 1. ECR processing parameters for Fe deposition
After catalyst deposition, CNTs were synthesized by homemade method. The schematic diagram of the self-designed equipment for CNTs synthesis with alcohol chemical vapor deposition (CVD) is shown in Fig. 2. The sizes of vacuum chamber and the heater are $\Phi 100 \times 150$ mm and $50 \times 30$ mm, respectively. The electrical resistance is taken as the heating resource. The alcohol in a ceramic container was placed under the heater, and the specimen was placed on the heater in the vacuum chamber. A DC power supplier was applied to heat the specimens in the vacuum ($1 \times 10^{-2}$ Pa) under 38~40 A.

![Figure 2. Equipment for CNTs synthesis](image)

2.2.2. Micropunching

The prepared pure titanium sheet was properly cleaned with acetone and pure ethyl alcohol to remove any possible contaminant, and it was carefully put into the microdie. Thereafter, specimens were punched by the microprocessing machine MP50 (made in Japan), with 20 pulses per minute and feedrate of 2 mm.

The effects of CNTs on the wear loss and the surface morphology of micropunch were investigated through confocal laser, scanning electron microscopy (SEM), digital balance, etc.

3. Results and discussion

3.1. SEM and TEM morphology of CNTs coated on micropunch

The synthesized CNTs are shown in Fig. 3. It demonstrates that the length of CNTs is about 15 μm. Moreover, CNTs are tightly compacted, which resulted in curve aligning. The relevant
TEM image is shown in Fig. 4, which shows that CNTs are multi-walled nanotubes and that the diameter of the synthesized MWCNT was about 3–5 nm.

Figure 3. Synthesized CNTs coated on micropunch

Figure 4. TEM image of synthesized CNTs

3.2. Wear loss of micropunches

The wear loss of non-CNT- and CNT-coated micropunches is shown in Fig. 5. It illustrates that the weight of both kinds of micropunches (each for 5 times) decreases with the increment in punching number in the initial stage, which means that the wear of both micropunches in the initial stage was significantly increased and that the effect of CNTs on the wear loss was not remarkable.

With the punching in progress, the wear of non-coated/coated micropunches is in the quasi-stable period with a little wear loss as shown in Fig. 5, especially for punching number from 500 to 1,200 for non-coated micropunches and from 450 to 1,400 for CNTs coated micropunches. In this period, the effect of CNTs on the wear loss of micropunch is obviously sound.

During the severe wear period, with the punching numbers increasing further, such as over 1,200 for non-coated micropunch and over 1,400 for CNTs coated micropunch, the wear of micropunch was increased distinctly (Fig. 5). At the same time, the effect of CNTs on the wear loss decreased.
Also, due to CNTs coated on micropunches, the start of quasi-stable period was advanced. On the contrary, the end of quasi-stable period was postponed, as shown in Fig. 5. It elucidates that the effective quasi-stable period is longer than that of non-coated micropunches. For CNT-coated micropunches, it is 1,400 – 450 = 950. By comparison, for non-coated micropunches, it is 1,200 – 500 = 700. Furthermore, the total wear loss of CNT-coated micropunches was lesser than that of non-coated micropunches. It demonstrates that the life of micropunch was improved or prolonged evidently.

3.3. Surface texture of CNT-coated micropunch

Figure 6 shows the surface textures of CNT-coated micropunches during various punching periods. Figure 6a shows the initial surface texture of CNT-coated micropunch (see point A in Fig. 5). Carbon nanotubes forest was synthesized and distributed successfully on the surface of micropunch and tangled mutually.

With the punching being in progress in the initial stage, the distribution of CNTs is shown in Fig. 6b (Point B in Fig. 5). It shows that CNTs distributed on the surface non-uniformly and that a bulk of CNTs attached on the surface by the punching rubbing effect. When the punching is in the quasi-stable period, the surface texture of micropunch is shown in Figs. 6c and 6d (See point C and D in Fig. 5). It illustrates that CNTs uniformly distributed on the micropunch surface where a transfer film was formed between micropunch and substrate (Ti foil) during the punching process. It is due to the formation of this transfer film at the contact region by rubbing of the CNT forest that CNTs or debris produced adhered to the micropunch surface (or the mating surfaces), thereby avoiding direct contact during the punching period and providing lubricant properties to the interface due to their graphitic nature. The results presented are in accordance with the results shown in Fig. 5, and they are promising for prolonging the life of micropunches.
With the increment in punching number, the surface texture of micropunch is shown in Figs. 6e and 6f (See point E and F in Fig. 5). It shows that CNTs distributed sparsely and disappeared finally (Fig. 6f). It is noted that the promising effect of CNTs was lost, which resulted in severe wear of the micropunch.

Figure 6. Surface texture of micropunch in various conditions
3.4. Profile of punched microholes

The diameter of the punched microhole by non-CNT-coated and CNT-coated micropunches was measured by LEXT confocal laser-OLS3000, as shown in Fig. 7. The relevant results (each for 5 times) are shown in Fig. 8. Compared with Figs. 5 and 6, it illustrates that for both cases (non-CNT-coated and CNT-coated micropunches), in the different wear conditions, the diameter of the punched microhole changed correspondingly. In the initial condition, the diameter obviously decreased with the increment in punching number.

When the punching process is in the quasi-stable period, the diameter of the punched microholes was kept relatively stable. With the punching number increasing further, the diameter was decreased remarkably. For CNT-coated micropunch, due to the lack of attached CNTs on the micropunch, the relevant wear characteristic is same as that of non-CNT-coated micropunch. Therefore, the serious wear of the micropunch appeared during the micropunching in the severe wear condition. Consequently, the diameter of the punched microholes decreased seriously.

Moreover, the results shown in Fig. 8 well agreed with the wear loss of micropunches in the punching period, as shown in Fig. 5.
3.5. Benefit of micropunching

Microtechnology encompasses the technological approach, directed to the miniaturization of components and systems, down to micrometer scale. The major goals are integration and increase in functionality of systems and devices while keeping the dimensions small. Microtechnological components, such as distributed holes, bear the potential to provide further functionality, for instance, in sensor technologies and in biomedical applications. One prominent example is the lab-on-chip technology wherein the analytical functionality of the chip is given by specific functionalized surfaces. Microsystems are going to play an important and critical role in application domains. The development of highly integrated microsystems necessitates the advancement of compatible assembly and joining techniques. Existing macrolevel techniques are adapted for downsizing the assembly of hybrid microsystems. The ever-increasing demands for smaller, higher-quality, and lower-priced products from almost all fields of industry, household equipment, and entertainment electronics require the optimization of existing techniques and the development of new methods for the customized manufacture of microsystems with higher precision.

However, current microdevices are mainly made of silicone or glass and are fabricated using photo-resist techniques and/or micro-machining and micro-molding techniques. It is well known that with these conventional technologies the mechanical properties of substrate will be seriously affected. During the processing, when the source energy is input into the substrate, the substrate suffers heating, melting, vaporizing, and solidifying. Consequently, the properties of substrate will be changed obviously, which cannot meet requirements of application afterwards. Meanwhile, chemicals taken in microfabrication are harmful to environments. In the eco-friendly viewpoint, the minimization of potential environmental and human health risks associated with the manufacture is crucial and urgent. The highlighted key issue is the exploration of new methods to lower the cost and produce large quantities that are more...
environmentally friendly. As an attractive promising technique, micropunch overcomes the above-mentioned drawbacks of the traditional technologies successfully. HAZ (heat-affected zone) is avoided, and chemicals are not employed. Meanwhile, the efficiency of microhole forming is remarkably improved. Moreover, the debris formed in the process of micropunching can be recycled. According to principles of green engineering, such as to ensure that all material and energy inputs and outputs are as inherently safe and benign as possible; to minimize depletion of natural resources; to strive to prevent waste; to create engineering solutions beyond current or dominant technologies; improve, innovate, and to invent (technologies) to achieve sustainability, micropunching with CNTs is not only beneficial to microfabrication but also encourages the replacement of existing technologies with new methods that are more environmentally friendly throughout their life cycles.

4. Mechanism of CNTs’ effect

The effect of coated CNTs on the micropunches was simulated by movable cellular automaton. The results are shown in Fig. 9. It demonstrates that at the beginning of micropunching, because CNTs adhesion to micropunch is relatively low, the coated CNTs are easily detached from the surface of micropunch as shown in Fig. 9b (green circle with dash line).

Figure 9. MCA simulation of micropunching with CNTs coating
With the micropunching processed further, the coated CNTs are detached from the surface with larger areas as shown in Figs. 9c and 9d. Consequently, only a small fraction of micropunch surface can remain with CNTs under the effect of friction between the substrate and the surface of micropunch. It soundly agrees with the results as shown in Fig. 6. Therefore, the ability of CNTs’ adhesion to the surface of the micropunch is crucial to the longevity of the micropunch. CNTs with higher adhesion to the micropunch surface are hardly detached from the surface. During micropunching, the CNTs attached that are uniformly distributed on the surface of micropunch are the ideal media between the substrate and micropunch to lower the friction coefficient. As a result, the wear of micropunch was decreased significantly and the life of micropunch was prolonged remarkably. Meanwhile, the CNT-coated micropunch with higher adhesion will be more promising for the microfabrication.

5. Conclusion

Carbon nanotubes (CNTs) coated on the WC/Co micropunch and its effect on its wear characteristic were studied. It shows that due to the formation of this transfer film at the contact region by rubbing of the CNT forest, the CNTs produced adhered to the micropunch surface (or the mating surfaces), thereby avoiding direct contact during the punching period and providing lubricant properties to the interface due to their graphitic nature. For CNT-coated micropunches, the punching number in the quasi-stable period is 950. By comparison, for non-coated micropunches, it is 700. In addition, the total wear loss of CNT-coated micropunches is lesser than that of non-coated micropunches. As a result, CNT-coated micropunch is evidently promising to improve or prolong the life of micropunch.

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