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ORIGINAL ARTICLE

Effects of carbon nanotubes on wear of WC/Co micropunches

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Abstract Punching has potential for mass production of microfeatures. Long lasting punches are critical to successful application of micropunching. This paper is focused on investigating the effects of carbon nanotubes (CNTs) on prolonging the tool life of WC/Co micropunches. CNTs were grown on some of the micropunches. Punching on Ti specimens was carried out using micropunches with and without CNTs. Wear loss and surface texture of the micropunches and the size of the punched holes were measured using confocal microscopy, scanning electron microscopy, digital balance, etc. Results suggested that, with CNTs, a protective layer was formed after the run-in stage. The protective layer could lengthen the useful life of the micropunch by up to 35 % without directly affecting the size of the punched holes.

Keywords Carbon nanotubes · Micropunch · Wear characteristic · WC/Co

1 Introduction

Carbon nanotubes (CNTs) [1, 2] are unique nanosystems with extraordinary mechanical and electronic properties, which are consequences of their unusual molecular structure. Single-walled carbon nanotubes (SWCNTs) are CNTs with wall thickness of one carbon atom. Multi-walled carbon nanotubes (MWCNTs) contain coaxial arrays of SWCNTs, with the diameter increasing from two to several tens of nanometers. MWCNTs can have very high aspect ratio [2].

Since the last decade, an enormous amount of work has been devoted to reveal structural, electrical, mechanical, and chemical properties of CNTs and to explore their interesting applications [3–10]. CNTs with their unique properties—high tensile and flexural strengths, high elastic modulus, and high aspect ratio—have been regarded as an attractive contender in tribological applications. Interesting results were reported with significant reduction in friction and wear rates in nanotube–polymers [11, 12], ceramics [13, 14], and metal composites [15, 16]. Theoretically speaking, friction coefficient between the walls of MWCNTs can be extremely low [17–19].

Ability to fabricate microholes in large quantities has potential applications in microchip packaging, inkjet printhead manufacture, biochip technologies, etc. Work in micropunching was reported by many investigators [20–23].

Strong and long lasting punches are crucial to successful application of micropunching. The cost of WC/Co micropunches is high. Moreover, due to wear of the micropunch, quality of the punched holes deteriorates significantly after about 1,000 punching shots [23].

A layer of CNT coating on the surface may greatly prolong the tool life of micropunches by reducing wear loss during punching and enhancing the wear resistance of the punches. The purpose of this paper is to investigate the effects of CNT coating on the tool life of WC/Co micropunches. Experimental materials and procedures are covered in the next section. Following that, wear loss, surface texture of the punches, and the size of the punched holes are reported and discussed. A conclusion is given in the end.

2 Experimental materials and procedures

CNT coating was initially developed by direct growth of CNTs on some of the micropunches. Punching experiments were then conducted using micropunches with and without CNT coating.

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2.1 Experimental material

Micropunches in the experiments were made by Ultrahardness Tools Company, Japan. The effective diameter of the micropunches was 150 μm. The micropunches were formed using 75 % WC and 25 % Co particles by volume and the mean size of the particles was 50 μm. The final form and size were then obtained through fine grinding. The surface texture of a micropunch was shown in Fig. 1.

Specimens for punching experiments were pure titanium sheets 200 μm in thickness.

2.2 Experimental procedures

2.2.1 CNT growth

Micropunches were cleaned by acetone and pure ethyl alcohol for contaminant removal prior to CNT growth/deposition.

Fe was needed as catalyst for CNT growth. Fe was deposited on the working section of the micropunch by electron cyclotron resonance (ECR). Processing parameters were listed in Table 1. During deposition, the remaining sections of the punches were covered by Al foil to avoid possible distribution of Co in the micropunch itself, as Ni, Co, and Fe and their alloys or compounds were also catalysts for the growth of CNTs [24, 25].

Subsequent to Fe deposition, micropunches were placed in a vacuum chamber for CNT growth. A schematic diagram of the setup was shown in Fig. 2. A micropunch was placed above the heater inside the chamber. The size of the vacuum chamber and the heater was Φ100×150 mm and Φ50×30 mm, respectively. Heating was based on electrical resistance. Ethanol in a ceramic container was put under the heater to provide alcohol source for chemical vapor deposition. Conditions for CNT growth were summarized in Table 2.

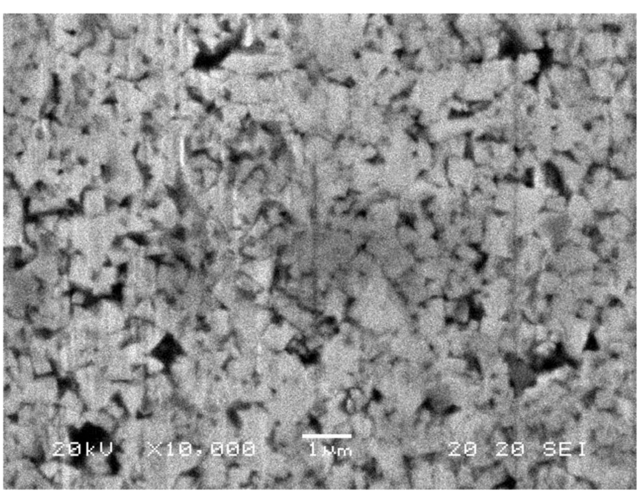


Fig. 1 Surface texture of a WC/Co micropunch

Table 1 ECR processing parameters for Fe deposition

Substrate	WC/Co micropunch
Catalyst	Fe
Irradiation time	60 s
Accelerated voltage	2,500 V
Ion current density	12.0 mA/cm^2
Gas	Ar
Gas flow rate	0.6 SCCM
Vacuum	1.5×10^{-4} Pa

2.2.2 Micropunching

Experiments were done using an MP50 punching machine. The titanium sheet was held between a pair of custom-made bushes during punching. Punching was done at a rate of 20 pulses per minute, and the sheet was advanced by 2 mm between pulses.

Wear of the punches and surface morphology were observed using confocal microscopy, scanning electron microscopy, etc. A digital balance was used to measure the weight loss of the micropunches.

3 Results and discussion

3.1 CNT-coated micropunch

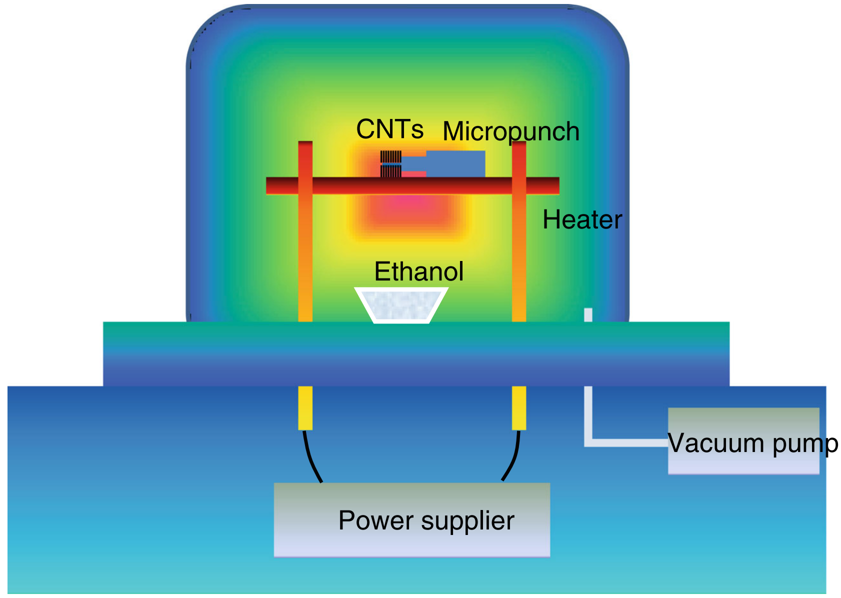
An image of a CNT-coated micropunch was shown in Fig. 3. CNTs were found to grow around the lateral and the end faces near the tip of the punch. The height of CNTs was about 15 μm. CNTs synthesized on the end face were shown in Fig. 4. The general growth direction was normal to the surface. They appeared wiggly, possibly because CNTs were tightly packed during growth. An image of one typical CNT was shown in Fig. 5. The image revealed that they were multi-walled nanotubes. The diameter was about 3–5 nm.

3.2 Wear loss of micropunches

Wear of the micropunches resulted in weight changes. Wear loss was assessed through intermittent weight measurement during punching. The weight profiles of punches with and without CNTs as they underwent 1,600 shots were shown in Fig. 6. The experiments were done five times and the profiles were based on averaged results.

For the micropunches without CNT coating, the weight profile could be divided into the initial stage, quasi-stable stage, and severe wear stage [23]. The initial stage of a micropunch (cycle no. <500) was the run-in stage. During this stage, the wear rate was relatively high. The surface was smoothened and crests were lowered. Then the punch entered

Fig. 2 Setup for CNT growth



the stage of quasi-stability (cycle no. 500–1,200) of very little wear loss and very little change to the surface texture. After that came the stage of severe wear (cycle no. >1,200). Loss of Co was acute in the beginning part of this stage. This resulted in fracture and detachment of WC particles from the punch, which accelerated the subsequent weight loss.

Figure 6 showed that the micropunches with CNT coating could also be characterized by the same three stages of wear. The main difference was that the quasi-stable stage started earlier and ended later (cycle no. 450–1,400).

3.3 Surface texture of CNT-coated micropunch

The surface texture of the CNT-coated micropunches during the progression of punching was shown in Fig. 7. The initial surface texture (point A, Fig. 6) before punching was shown in Fig. 7a. As seen from the top of the CNT forest, CNTs were densely populated and got tangled up.

In the middle of the initial stage (point B, Fig. 6), the CNTs had basically been broken down after the micropunch was forced in and out of the specimen for hundreds of times. Pieces of CNTs were attached to the surface of the micropunch (Fig. 7b). Some of the pieces were submicron in size, but some could be more than 10 μm in length and over 3 μm across.

Table 2 Parameters for CNT growth

Heating rate	3–4 A/s
Cooling rate	5 A/s
Reaction direct current	38–40 A
Reaction time	10 s
Vacuum	1×10^{-2} Pa

The two weight profiles looked almost the same in the initial stage in Fig. 6. It seemed that the CNTs had very little effect on the weight loss during the run-in of the punches—the crests on the surface of the CNT coated punch were lowered just as those on the surface of the punch without CNT coating.

Weight loss continued throughout the initial stage. One expected some CNT pieces attached to the surface of the micropunch were also detached from the punch together with the base material. However, some loosened CNT pieces were subsequently re-attached to the surface of the punch.

Wear loss almost halted after about 450 shots as the micropunch entered the quasi-stable stage. Figure 7c–d showed the surface texture of the micropunch in the early part and about two third into the quasi-stable stage (points C and D, Fig. 6). According to these two images, there were very little change to the size and distribution of CNT attachments

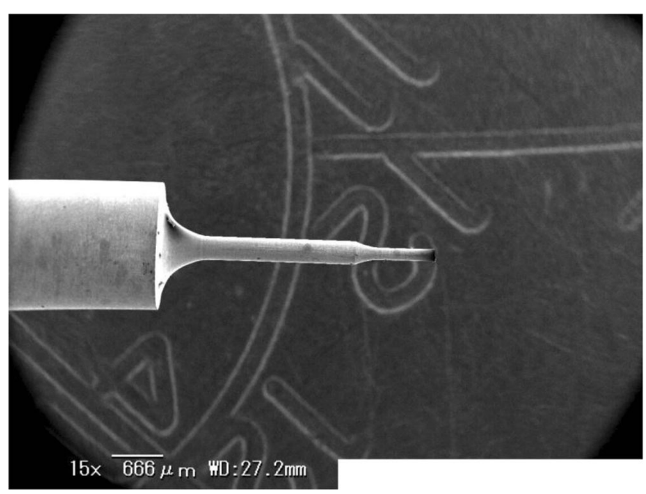


Fig. 3 A micropunch with CNT coating

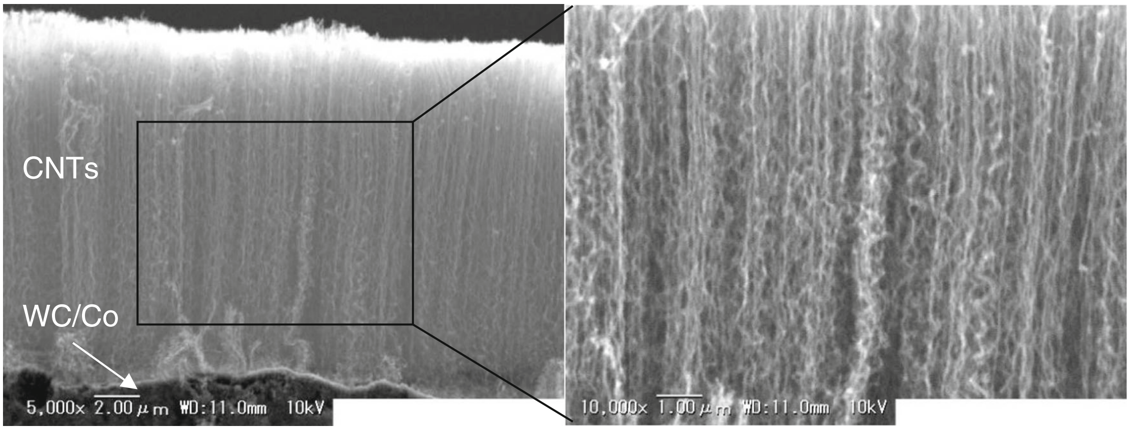


Fig. 4 CNTs on the end face of micropunch

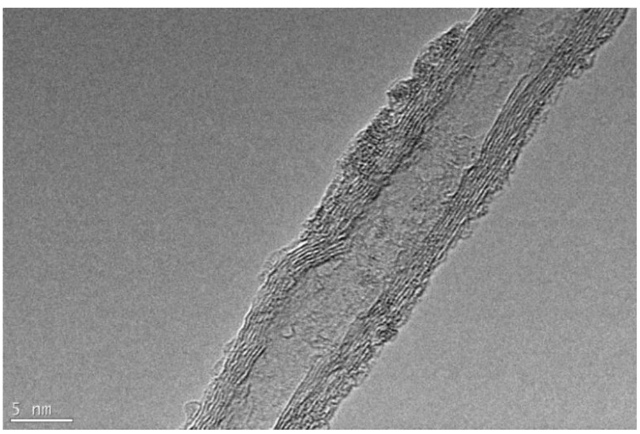


Fig. 5 TEM image of a CNT

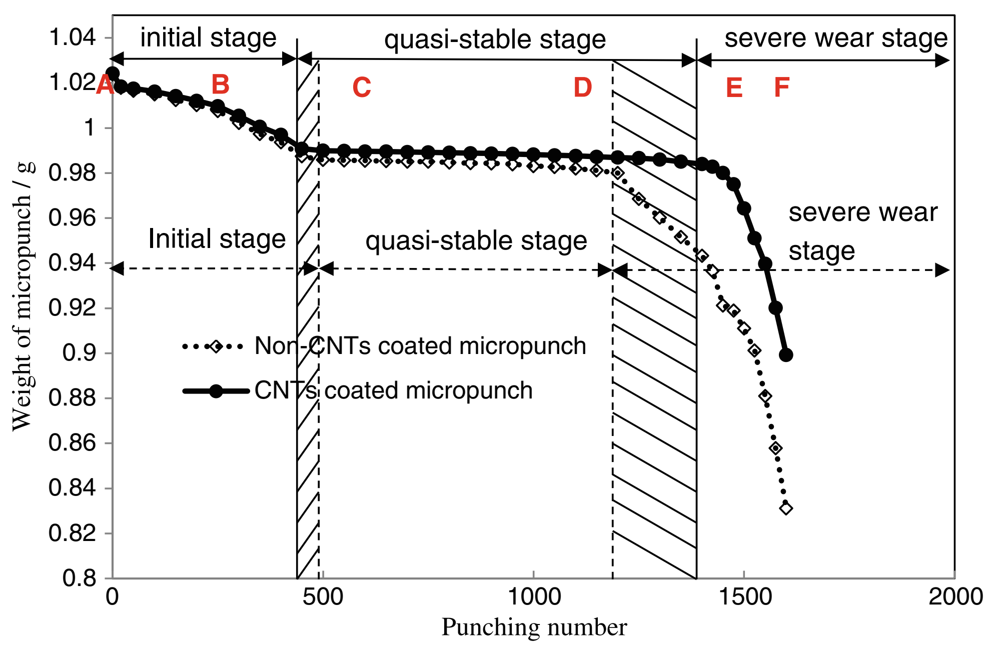
on the surface. Basically, CNTs remained abundant on surface of the micropunch up to point D.

According to Fig. 6, wear loss of the micropunch without CNT coating was small in the quasi-stable stage. The surface was relatively smooth after the initial run-in. The combined effects of WC and Co were able to resist wear due to punching.

Comparing the two profiles in Fig. 6, one could see that wear loss of the micropunch with CNT coating was smaller in the quasi-stable stage, and the duration of the quasi-stable stage was also longer. It seemed that CNTs formed a protective layer that prevented wear of the punch. This protective layer prevented direct contact between base material of the micropunch and the specimen as the punch was forced through the specimen. It also provided lubrication during punching by virtue of the graphitic nature of CNTs [26, 27].

Surface texture of the micropunch at the onset of the severe wear stage (point E, Fig. 6) was shown in Fig. 7e. CNTs were

Fig. 6 Weight of micropunches during punching



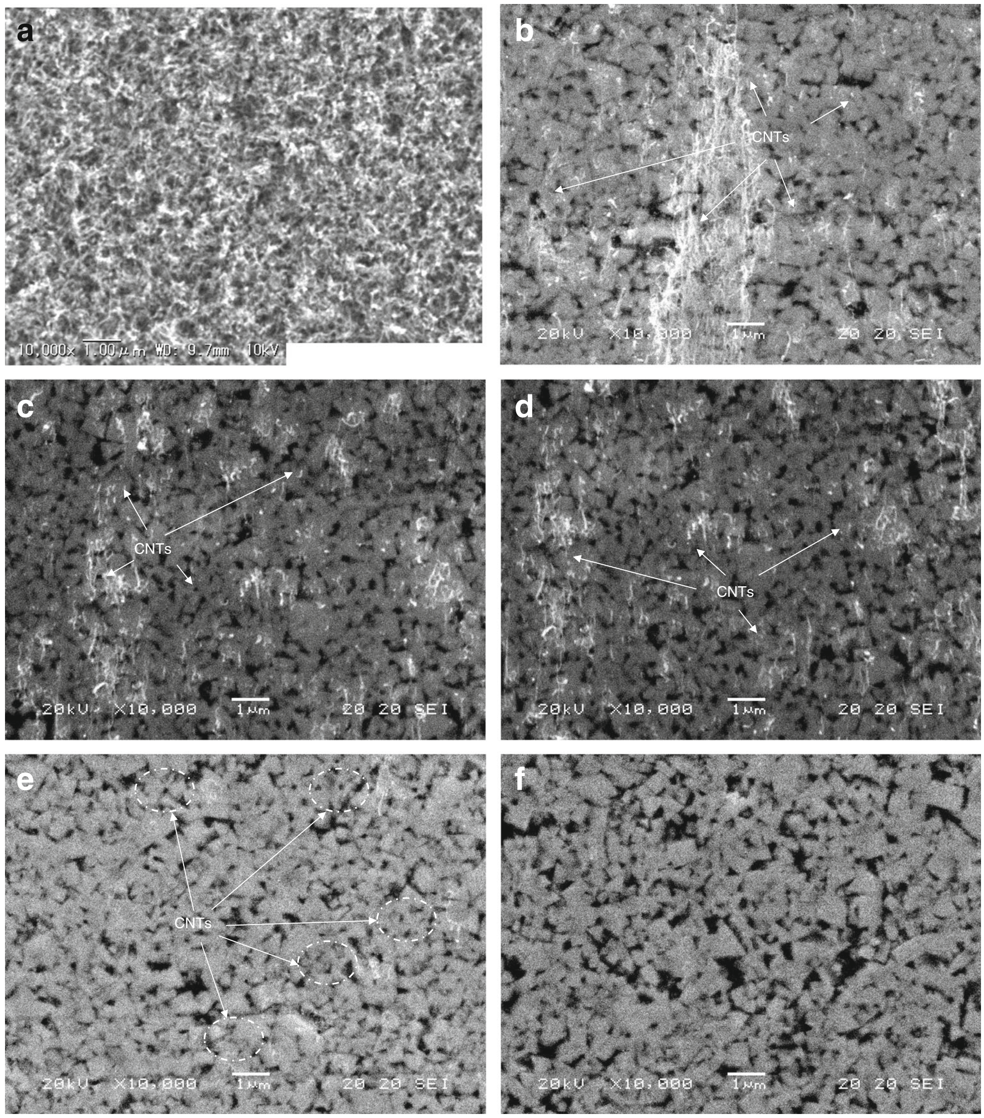


Fig. 7 Surface texture of the CNT coated micropunch during punching. **a** Before punching. **b** Middle of the initial stage. **c**–**d** Early part and two third into the quasi-stable stage. **e**–**f** Onset of the severe wear stage and deeper into the severe wear stage

only sparsely distributed and the size of the CNT pieces was quite small. This suggested that the layer of protective layer was almost worn off by the end of the quasi-stable stage.

Deeper into the severe wear stage (point F, Fig. 6), traces of CNT were no longer present on the micropunch (Fig. 7f). Outline of the WC particles was clearer than before,

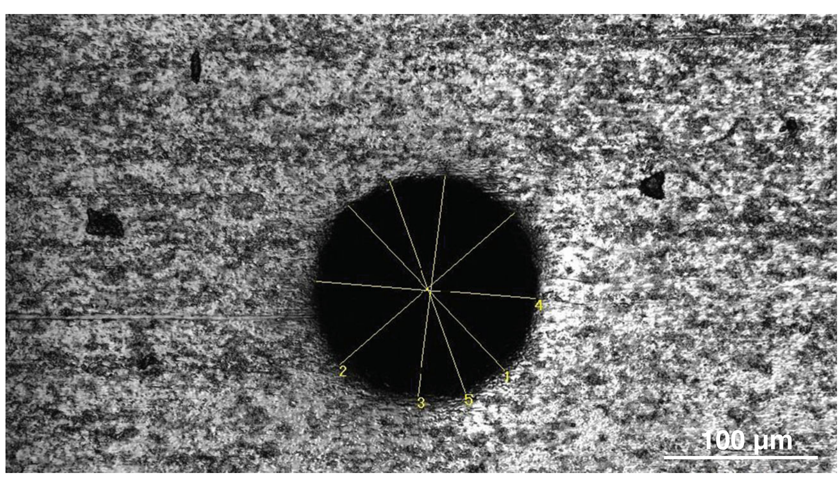


Fig. 8 Measurement of microhole

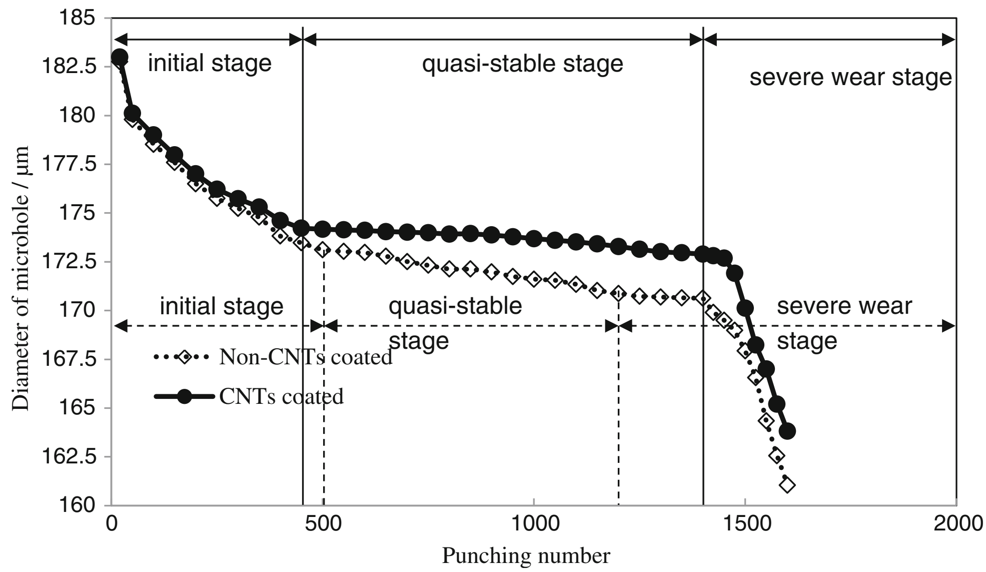


Fig. 9 Diameter of microholes during punching

suggesting that much of the Co near the surface of the micropunch had also been worn off. Rapid weight loss was attributed to loss in WC, due to direct exposure to WC protrusions to punching wear after the worn off of the CNT layer, and due to the loss of Co which had helped to bind the WC particles together.

3.4 Profile of punched microholes

Microholes were obtained by punching with and without CNT-coated micropunches. The diameter of the holes was measured using a LEXT confocal laser-OLS3000 microscope as shown in Fig. 8. The relevant results (each from the average of five measurements) were shown in Fig. 9.

During the initial stage, the diameter profile of the two punches in Fig. 9 essentially overlapped, just as the weight profiles in Fig 6 overlapped. There was a marked reduction of the diameter of the holes as the wear loss was fast in this run-in stage. CNTs had little effects on the size of the hole in this stage. The size depended mainly on the weight of the micropunch.

Only a small reduction of the diameter of the hole was experienced in the quasi-stable stage for both punches, as the weight loss was also small during this stage. The diameter reduced slightly faster for the punch without CNT coating, which was consistent with the slightly faster weight reduction of the corresponding punch. The hole size was reduced from 174.2 to 172.9 μm for punching with CNT coating, and was from 173.1 to 170.9 μm without CNT coating. The holes produced by the CNT-coated micropunches were slightly bigger mainly because of the slightly earlier onset of the quasi-stable stage for the CNT-coated micropunches.

The hole size reduction was rapid in the stage of severe wear. After 1,600 shots, the diameter was reduced to 163.8 μm for punching with CNT coating; it was reduced to 161.0 μm without CNT coating. These represented about 6 % reduction from the nominal diameter in the quasi-stable stage.

Near the end the reduction rate was about 6.5 μm per 100 shots for both punches.

4 Conclusion

A dense layer of CNTs was grown on the working regions of WC/Co micropunches. The diameter of the micropunches was 150 μm, and the average height of the CNTs was 15 μm.

In the course of punching, the weight profile of CNT-coated micropunches could be divided into the initial run-in stage, quasi-stable stage, and severe wear stage, just like the case of micropunches without CNT coating.

The micropunch was smoothened during the initial run-in stage. Presence of CNTs had little influence of the run-in. The weight profile of the micropunch with and without CNTs essentially overlapped.

Pieces of CNT were seen attached to the micropunch during the run-in stage and the quasi-stable stage.

In the end of the run-in stage and after the micropunch had been sufficiently smoothened, CNTs formed a protective layer and helped to extend the quasi-stable stage by about 250 shots (or 35 % of the original length without CNT coating).

The diameter of the punched holes corresponded to the weight of the micropunch, as indicated by the close correspondence between the profile of the weight of the punch and that of the diameter of the punched holes.

CNT coating helped to lubricate the micropunch and specimen interface. It did not directly influence the size of the punched holes.

The quasi-stable stage of the CNT coated punch was from cycle nos. 450 to 1400. That of the punch without CNT coating was from cycle nos. 500 to 1200. These implied that the CNT coating could extend the length of the quasi-stable stage by about 250 shots (or 35 %).

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References

1. Iijima S (1993) Single-shell carbon nanotubes of 1-nm diameter. Nature 363:603–605
2. Iijima S (1991) Helical microtubules of graphitic carbon. Nature 354: 56–58
3. Boncel S, Müller KH, Skepper JN, Walczak KZ, Koziol KKK (2011) Tunable chemistry and morphology of multi-wall carbon nanotubes as a route to non-toxic, theranostic systems. Biomaterials 32:7677–7686
4. Gutierrez F, Rubianes MD, Rivas GA (2012) Dispersion of multi-wall carbon nanotubes in glucose oxidase: characterization and analytical applications for glucose biosensing. Sensors Actuators B 161: 191–197
5. Tofighy MA, Mohammadi T (2011) Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. J Hazard Mater 185:140–147
6. Upadhyayula VKK, Gadhamshetty V (2010) Appreciating the role of carbon nanotube composites in preventing biofouling and promoting biofilms on material surfaces in environmental engineering: a review. Biotechnol Adv 28:802–816
7. Tiusanen J, Vlasveld D, Vuorinen J (2012) Review on the effects of injection moulding parameters on the electrical resistivity of carbon nanotube filled polymer parts. Compos Sci Technol 72:1741–1752
8. Alig I, Pötschke P, Lellinger D, Skipa T, Pegel S, Kasaliwal GR, Villmow T (2012) Establishment, morphology and properties of carbon nanotube networks in polymer melts. Polymer 53:4–28
9. Bhattacharya M, Hong S, Lee D, Cui T, Goyal SM (2011) Carbon nanotube based sensors for the detection of viruses. Sensors Actuators B 155:67–74
10. Kasel D, Bradford SA, Šimůnek J, Heggen M, Vereecken H, Klumpp E (2012) Transport and retention of multi-walled carbon nanotubes in saturated porous media: effects of input concentration and grain size. Water Res 1–12
11. Pöllänen M, Pirinen S, Suvanto M, Pakkanen TT (2011) Influence of carbon nanotube-polymeric compatibilizer masterbatches on morphological, thermal, mechanical, and tribological properties of polyethylene. Compos Sci Technol 71:1353–1360
12. Green MJ, Behabtu N, Pasquali M, Adams WW (2009) Nanotubes as polymers. Polymer 50:4979–4997
13. Zhan GD, Kuntz JD, Wan JL, Mukherjee AK (2003) Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites. Nat Mater 2(1):38–42
14. Hvizdoš P, Puchý V, Duszová A, Dusza J, Balázsi C (2012) Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. Ceram Int 38:5669–5676
15. Guiderdoni C, Pavlenko E, Turq V, Weibel A, Puech P, Estournès C, Peigney A, Bacsa W, Laurent C (2013) The preparation of carbon nanotube (CNT)/copper composites and the effect of the number of CNT walls on their hardness, friction and wear properties. Carbon 58: 185–197
16. Bakshi SR, Keshri AK, Agarwal A (2011) A comparison of mechanical and wear properties of plasma sprayed carbon nanotube reinforced aluminum composites at nano and macro scale. Mater Sci Eng A 528:3375–3384
17. Damnjanović M, Vuković T, Milosević I (2002) Super-slippery carbon nanotubes: symmetry breaking breaks friction. Eur Phys J B 25: 131–134
18. Dickrell PL, Sinnott SB, Hahn DW, Raravikar NR, Schadler LS, Ajayan PM, Sawyer WG (2005) Frictional anisotropy of oriented carbon nanotube surfaces. Tribol Lett 18(1):59–62. doi:10.1007/s11249-004-1752-0
19. Dickrell PL, Pal SK, Bourne GR, Muratore C, Voevodin AA, Ajayan PM, Schadler LS, Sawyer WG (2006) Tunable friction behavior of oriented carbon nanotube films. Tribol Lett 24(1):85–90
20. Joo BY, Rhim SH, Oh SI (2005) Micro-hole fabrication by mechanical punching process. J Mater Process Technol 170(3):593–601
21. Brousseau EB, Dimov SS, Pham DT (2010) Some recent advances in multi-material micro- and nano-manufacturing. Int J Adv Manuf Technol 47:161–180
22. Fonda P, Katahira K, Kobayashi Y, Yamazaki K (2012) WEDM condition parameter optimization for PCD microtool geometry fabrication process and quality improvement. Int J Adv Manuf Technol 63:1011–1019
23. Guo W, Tam HY (2011) Effects of extended punching on wear of the WC/Co micropunch and the punched microholes. Int J Adv Manuf Technol 59:955–960. doi:10.1007/s00170-011-3567-0
24. Esconjauregui S, Whelan CM, Maex K (2009) The reasons why metals catalyze the nucleation and growth of carbon nanotubes and other carbon nanomorphologies. Carbon 47:659–669
25. Dupuis AC (2005) The catalyst in the CCVD of carbon nanotubes—a review. Prog Mater Sci 50:929–961
26. Hu JJ, Jo SH, Ren ZF, Voevodin AA, Zabinski JS (2005) Tribological behavior and graphitization of carbon nanotubes grown on 440C stainless steel. Tribol Lett 19(2):119–125
27. Abad MD, Sánchez-López JC, Berenguer-Murcia A, Golovko VB, Cantoro M, Wheatley AEH, Fernández A, Johnson BFG, Robertson J (2008) Catalytic growth of carbon nanotubes on stainless steel: characterization and frictional properties. Diam Relat Mater 17: 1853–1857