Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 22(2012) 2719−2725
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

# Preparation and tribological performances of Ni−P−multi-walled carbon nanotubes composite coatings

MENG Zhen-qiang, LI Xi-bin, XIONG Yong-jun, ZHAN Jing

State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Received 28 November 2011; accepted 26 October 2012

**Abstract:** Multi-walled carbon nanotubes (MWNTs) were wet-milled in the presence of ammonia and cationic surfactant and then used as reinforcements to prepare Ni−P−MWNTs composite coatings by electroless plating. The tribological performances of the composite coatings under dry condition were investigated in comparison with 45 steel and conventional Ni−P coating. Micrographs show that short MWNTs with uniform length and open tips were obtained through the wet-milling process. The results of wear test reveal that the Ni−P−MWNTs composite coatings posses much better friction reduction and anti-wear performances when compared with 45 steel and Ni−P coating. Within the MWNTs content range of 0.74%−1.97%, the friction coefficient and the volume wear rate of the composite coatings decrease gradually and reach the minimum values of 0.08 and $6.22\times10^{-15}$ $m^3/(N\cdot m)$, respectively. The excellent tribological performances of the composite coatings can be attributed to the introduction of MWNTs, which play both roles of reinforcements and solid lubricant during the wear process.

**Key words:** Ni−P coating; carbon nanotubes; composite coating; ball milling; electroless plating; self-lubrication; tribological performance; friction coefficient; volume wear rate

## 1 Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by IIJIMA [1], lots of researches on the structures and properties have been done. According to theoretical calculations and in-situ measurements, CNTs have exceptional optical, electrical and mechanical properties, which predicate that CNTs possess promising applications in many fields such as physics, chemistry and materials [2−4]. Considered as the strongest fiber [5], CNTs have elastic modulus as high as 1.8 TPa and the tensile strength reaches 67 GPa. Moreover, because of the closed tubular structure of graphite sheets, CNTs are expected to form the desirable weak interaction with the contacting couple during wear process [6]. Thus, more and more studies have been investigated to use CNTs to prepare composite materials with excellent tribological performances [7−9].

However, the poor dispersion of CNTs is an urgent problem to be solved due to their high length-diameter ratio and their van der Waals interactions [10]. To improve the dispersion, most researchers aimed to functionalize CNTs with various chemical groups [11, 12], but less attention was paid to cutting CNTs by ball milling. Ball milling is a mechanical process during which the high-pressure is generated locally by the collision of milling balls. Many researchers [13,14] found that milling CNTs under dry condition, alone or with other powder, can substantially reduce the length of CNTs. Accordingly, good dispersion is available due to a mild entanglement degree of CNTs. CHEN et al [15] and DENG et al [16] have used the dry-milled CNTs to prepare Ni−P based composite coating by electroless plating, which shows desirable tribological performances under the lubrication condition. Recent researches indicated that the CNTs obtained by wet-milling have more open tips and functional groups than those obtained by dry-milling [17,18]. These features are effective to enhance the wettability and thus improve the dispersion of CNTs in aqueous solution.

In this work, multi-walled carbon nanotubes (MWNTs) were wet-milled in the presence of a new milling medium. The milling effect was studied in comparison with ordinary dry-milling. The wet-milled MWNTs were used as reinforcements to prepare

**Foundation item:** Project (JPPT-115-5-1759) supported by the National Defense Science and Technology Industry Committee of China; Project (20090162120080) supported by Research Fund for the Doctoral Program of Higher Education of China; Project (2010FJ3012) supported by the Program of Science and Technology of Hunan Province, China
**Corresponding author:** XIONG Yong-jun; Tel: +86-731-88876566; E-mail: yongjunxiong@csu.edu.cn
DOI: 10.1016/S1003-6326(11)61523-9

Ni−P−MWNTs composite coatings by electroless plating. The tribological performances of the composite coatings under dry condition were investigated and the mechanism was discussed. The tribological performances of conventional Ni−P coating and 45 steel were also tested for comparative purpose.

## 2 Experimental

### 2.1 Milling of MWNTs

MWNTs used in the study were prepared by a catalytic chemical vapor deposition (CVD) method with purity higher than 95%, 1−2 μm in length and 20−40 nm in outer diameter. Milling experiments were carried out in a planetary ball milling apparatus. To obtain wet-milled MWNTs, 2.0 g of MWNTs, 0.5 g of cetyltrimethyl benzyl ammonium bromide (CTAB), 60 g of ammonia, and 100 g of milling ball (GCr15 steel) were put into a stainless steel container. The container was then rolled at a rotor speed of 300 r/min for 6 h. After ball milling, MWNTs were purified in 4 mol/L $HNO_3$ at 80 °C for 0.5 h, followed by centrifugation, repeated washing with deionized water until pH>6.5 and drying. Dry-milled MWNTs were also obtained through a similar process for comparative purpose. The sole difference from the wet-milling process is that MWNTs were milled under dry condition and none of ammonia or CTAB was involved. The morphological characteristics of MWNTs, before and after millings, were observed using a JEM−2100F transmission electron microscopy (TEM).

### 2.2 Preparation of Ni−P coating and Ni−P−MWNTs composite coatings

In the present study, 45 steel was adopted as the substrate for the plating of Ni−P−MWNTs composite coatings. The basic bath compositions are listed in Table 1. To improve the bonding force between the composite coatings and the steel substrate, a Ni−P interlayer coating was firstly deposited for 0.5 h on the substrate. Then, Ni−P−MWNTs composite coatings were deposited for 3 h on the interlayer coating. In order to obtain different composite coatings, six concentrations of MWNTs in the plating bath (0.1, 0.3, 0.4, 0.5, 0.6 and 0.7 g/L) were adopted in the experiments. During the course of plating, the temperature of the bath was held at (87±1) °C and pH was maintained at 4.6±0.1. Meanwhile, agitation was used to disperse MWNTs in the plating bath.

Ni−P coating was also prepared with a similar bath composition and operating parameters. In order to avoid hydrogen brittleness and increase the hardness, the as-prepared Ni−P−MWNTs composite coatings and Ni−P coatings were annealed in vacuum at 400 °C for 1h before the wear test.

The surface and cross-section morphological features of the Ni−P−MWNTs composite coating were investigated by a JSM−6360LV scanning electron microscopy (SEM) and a MeF3A optical microscopy, respectively. The contents of MWNTs in the composite coatings were tested using a LECO/CS−600 carbon-sulfur analyzer.

**Table 1** Bath compositions for electroless plating

| Chemical composition | Concentration/(g·L$^{-1}$) |
|---|---|
| $NiSO_4·6H_2O$ | 21 |
| $NaH_2PO_2·H_2O$ | 24 |
| $CH_3CH(OH)COOH$ | 30 |
| $PbCl_2$ | $1\times10^{-3}$ |
| $C_{16}H_{33}(CH_3)_3NBr$ | 0. 5 |

### 2.3 Friction and wear tests

The tribological experiments of 45 steel, Ni−P coating and the composite coatings were performed using a reciprocating ball-on-flat tribometer (UMT−3, CETR, USA) under dry condition in ambient air. The relative humidity was 45%−50% and the temperature was 20−25 °C. Standard GCr15 steel balls (*d*9.5 mm) were used to slide against the samples over a wear track of 6.0 mm with a speed of 0.1 m/s. The applied load was 10 N and the test time was 0.5 h. The friction coefficients were recorded throughout the tests. The cross-sectional areas of wear tracks were measured using a profilometer and the volume losses were calculated with the help of corresponding software. The worn surfaces of the tested samples were observed by SEM. The elemental information of the worn surface of the steel ball sliding against the Ni−P−MWNTs composite coatings were also analyzed by a K-Alpha 1063 X-ray photoelectron spectrometer (XPS).

## 3 Results and discussion

### 3.1 Morphology and structure of MWNTs

TEM images of MWNTs are shown in Fig. 1. The MWNTs before milling (Fig. 1(a)) are long, curved and entangled together, while the milled MWNTs are obviously shorter. Compared with the dry-milled MWNTs (Fig. 1 (b)), the wet-milled MWNTs (Fig. 1 (c)) are more uniform in length. The milling medium seems to play a key role for the differences between the dry-milled and wet-milled MWNTs. During the course of dry-milling, MWNTs tend to be compacted by the milling balls and form large agglomerates [17]. When impacts are generated on the agglomerates, MWNTs of the outer part adsorb the majority of the collision energy. As a result, MWNTs of the inner part of the agglomerates are not easy to crack, while MWNTs of the