Effects of carbon nanotube concentration and nickel matrix crystalline on the elastic modulus of nickel-based composite coatings

Tsunehisa Suzuki*, Kazushi Yokoyama*, Mutsuto Kato*, Hiroshi Iizuka**

(Received on January 16, 2015)

* Yamagata Research Institute of Technology, Yamagata, 990-2473, Japan
** Department of Mechanical Engineering, Yamagata University, Yonezawa Yamagata, 992-8510, Japan

Abstract

The effects of carbon nanotube (CNT) composites on the elastic modulus of nickel-based CNT composite coating were investigated using the indentation method. The elastic moduli of the coating at CNT concentrations of 0–40 vol.% were evaluated by experimentation and numerical calculations. The elastic modulus was changed by the addition of CNTs because of changes in CNT composites and nickel crystal. The structure of the matrix changed from the columnar crystal to random crystal due to the addition of the CNTs. The elastic modulus of the coatings with low concentration of CNTs can be calculated by the rule of mixtures from the percentage of each crystal orientation and the value of elastic moduli of each crystal orientation, and were almost the same as the experimental value. The measured elastic moduli agree well with the predictions of Halpin–Tsaï equations at low CNT concentrations in the matrix. The high-CNT-concentration layer, which is approximately 40 vol.%, can be prepared by periodic reverse electroplating. The coatings with a surface layer of high CNT concentration have a higher elastic modulus. Although the moduli increase with increasing CNT concentrations, the determined values are lower than the predicted values of elastic modulus derived from the Halpin–Tsaï equations.

Key words: Carbon nanotubes (CNTs), Elastic modulus, electroplating, composite coatings.

1. INTRODUCTION

Carbon nanotubes (CNTs) are reinforcements for metallic, ceramic, and polymer composites due to their high elastic modulus [1, 2]. Recent studies have shown that the elastic modulus of CNT ranges between 300 and 1500 GPa [1, 2]. The high strength is the result of the near-perfect structure and the strong sp2 bonding between the carbon atoms. Therefore, metal matrix CNT composites have a great potential in load bearing applications [3].

Metal matrix CNT composites are fabricated by powder metallurgy techniques, melt processing, electrochemical techniques, and other novel techniques. Electrochemical techniques are useful for partial improvement of the surface property. Some recent researches have reported that friction and wear properties of Ni-based CNT composite coatings can be improved by codepositing CNTs in the matrix [4]. We have also investigated the improvement in the tool life of the electroplated diamond tools due to the application of Ni-based CNT composite coatings [5] and in wear resistance of electrical discharge machining electrodes due to the application of Cu-based CNT composite coatings [6, 7]. However, the effects of CNT concentration and nickel matrix crystalline on elastic modulus of nickel-based CNT composite coatings and the mechanism of increasing the elastic modulus of the composite coatings prepared by electroplating are unclear.

Furthermore, the effects of CNT composites on the elastic modulus of nickel-based CNT composite coating were investigated in this study using the indentation method. Especially, the hardness and elastic modulus of the coatings with high CNT concentrations layers were experimentally and mathematically evaluated and high-concentration-CNT layers were obtained by periodic reverse (PR) electroplating [8–11]. The use of PR electroplating greatly enhances CNTs into a nickel matrix and increases the CNT concentration [11].

First, nickel-based CNT composite coatings with low concentrations of CNTs were fabricated by direct current (DC) electroplating and the coatings with high concentrations of CNTs were fabricated by PR electroplating. The elastic modulus of each coating was measured by the indentation method. Subsequently, the elastic moduli were compared in terms of CNT concentrations and nickel matrix crystalline by applying the rule of mixtures to the CNTs and nickel matrix crystals. Additionally, the mechanism of improving the elastic modulus has been discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Electroplating methods

Table 1 lists the bath composition and operational conditions of the plating of the nickel-based CNT composite coatings. Nickel-based CNT composites
were deposited on tungsten carbide substrates by a method of electroplating that uses a nickel sulfamate plating bath to add 1–10 g/L CNTs under galvanostatic conditions. The CNTs used in this study were multi-walled (NC7000, Nanocyl) and were typically 9.5 nm in average diameter and 1.5 μm in average length. Tungsten carbide substrates were used as anodes and a pure nickel plate was used as the cathode. The temperature of the plating bath was maintained at 45 °C. During electroplating, the horn sonication method \(^{12}\) was used to generate ultrasonic vibration (24 kHz, 150 W) in the plating bath for the enhancement of CNT dispersion. For DC electroplating, current density was controlled at 5 A/dm\(^2\) by a galvanostat.

Figure 1 shows the current density waveform of PR electroplating. The conditions were as follows: frequency = 250 mHz, duty = (anodic time \(T_{ON}\)/cathodic time \(T_{REV}\)) = 9/1, anodic current \(I_{ON}\) = –1 A/dm\(^2\), and cathodic current \(I_{REV}\) = 6 A/dm\(^2\).

### 2.2. Characterization of the coatings

For characterization of the hardness and elastic modulus of the coatings, load–displacement curves for the coatings were measured by a dynamic hardness tester (DUH-200, Shimadzu, Japan). The conditions for the measurement were as follows: maximum load = 98 mN, load speed = 2.65 mN/s, keeping time = 5 s, and probe tip = Berkovich 115-deg diamond-tip. The dynamic hardness of the coatings was calculated by maximum load \(P_{MAX}\) [mN] and maximum displacement \(d_{MAX}\) [μm] using the following equation\(^{13}\):

\[
DH = 3.8584 \frac{P_{MAX}}{d_{MAX}^2}
\]

Elastic modulus of the coatings was calculated by slopes of load–displacement curve for unloading at a rate of 0–30%. The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα radiation. Crystal orientation of the nickel matrix was determined by X-ray diffraction (XRD).

### 3. RESULTS AND DISCUSSION

#### 3.1. Volume fraction of CNTs in nickel-based CNT composite coatings

Figure 2 shows the SEM image of the surface of a nickel-based CNT composite coating formed by PR electroplating. A number of CNTs embedded in nickel

---

**Table 1** Electroplating bath composition and operating conditions (\(T_{ON}\): anodic time, \(T_{REV}\): cathodic time, \(I_{ON}\): anodic current density, \(I_{REV}\): cathodic current density)

| Bath                  | Ni(NH\(_4\))\(_2\)SO\(_4\): 5H\(_2\)O: 500 g/L, NiCl\(_2\): 4H\(_2\)O: 4 g/L, H\(_2\)BO\(_3\): 33 g/L |
|-----------------------|--------------------------------------------------------------------------------------------------|
| Agitation             | Horn sonication method\(^{12}\)                                                                 |
| Bath temperature      | 45 °C                                                                                             |
| Current density       | DC: \(I_{ON}\) = –5 [A/dm\(^2\); PR: \(I_{ON}\) = –1/6 [A/dm\(^2\); \(T_{ON}/T_{REV}\) = 3.6/0.4 [sec], 250 mHz |
| Process time          | DC: 60 min, PR: 240 min                                                                          |
| Substrate             | Micro fine grade cemented tungsten carbide                                                         |

---

**Fig. 1** Current density waveform of periodic reverse electroplating for high-concentration carbon nanotube composite coatings.

**Fig. 2** SEM image of nickel-based CNT composite coating formed by PR electroplating.

**Fig. 3** XPS depth profiles of Cls for the nickel-based CNT composite coatings prepared by DC and PR electroplating under the condition that amount of CNTs in the plating bath is 1 g/L.
matrix can be observed in this figure. Most nickel crystals are tens of nm in diameter, which decreases with the addition of CNTs.

Figure 3 shows XPS depth profiles of C1s for the CNT composite coatings. The volume fraction of carbon is similar to that of the CNTs. The depth is calculated by Ar sputtering time and sputtering rates for carbon and nickel. The volume fraction of CNTs in PR electroplatings is much higher than that in DC electroplatings. PR electroplatings have a high-concentration CNT composite layer at the surface, within the thickness of 1–2 μm.

### 3.2. Dynamic hardness and elastic modulus measured by indentation methods

Figure 4 shows the typical load–displacement curves of the coatings. Figures 5 and 6 show the variation in the dynamic hardness and elastic modulus, respectively, with varying amounts of CNTs in a plating bath. Each experiment was repeated at least five times. The error bars here represent standard deviations.

Dynamic hardness of the DC coatings fabricated by DC electroplating increases rapidly up to 2 g/L, decreasing gradually thereafter. The dynamic hardness of the DC coating at 2 g/L is 571 DH115 and almost three times as hard as that of a pure nickel coating. The elastic modulus of the DC coatings also increases up to 1–2 g/L, decreasing gradually thereafter. From these results, it can be stated that the DC coating has the highest dynamic hardness and highest elastic modulus at 1–2 g/L CNTs.

Dynamic hardness of the PR coating, which is a product of PR electroplating, is lower than that of DC coating at 1 g/L CNTs. On the other hand, the elastic modulus of the PR coating is higher than that of the DC coating at 1 g/L CNTs. The slope of load–displacement curve in the PR coating at low load ranges is much gentler than that at high load ranges as shown in Fig. 4. This result indicates that the soft layer is absent at PR coating surface. Figure 3 shows XPS depth profiles of C1s for DC coating and PR coating electrodeposited by the bath adding 1 g/L CNTs. The carbon composition of the PR coating is much higher than that of the DC coating at the surface. This result indicates that CNT concentration at the surface is high, especially for PR coating. The CNT concentration at the surface was so high that the porous structured layer was formed at the surface, and dynamic hardness was decreased due to the soft porous layer containing a number of CNTs. The soft layer did not influence the elastic modulus measurements much because the elastic modulus was calculated by the slope of the load–displacement curves at the high load range. The high elastic modulus of PR coatings is considered to be due to high CNT concentration that was increased by the measurement load.

### 3.3 Effects of nickel crystal structure on elastic modulus

Figure 7 shows a plot of the XRD orientation index of the surface of nickel-based coatings with different CNT concentrations. The orientation index was calculated using the Wilson formula 14). An
orientation index of 1 indicates a random crystal structure. Normal nickel coatings had columnar crystal structures, whereas Nickel-based CNT composite coatings had a random crystal orientation.

Figure 8 shows a cross-sectional schematic of nickel crystal structures with/without CNTs derived from the results of the XRD analysis. The mechanism of the changes in the nickel matrix crystal structure owing to the addition of CNTs is discussed here. In the case of normal nickel electroplating without additives, XRD analysis indicated preferential growth of the electroplated nickel in the (200) plane direction, shown in Fig. 7, in the form of columnar structures. In the case of nickel electroplating with CNTs, which existed at the growth surface of nickel, the growth process of the nickel coatings was completely different. CNTs immediately become nickel nucleation sites after they touch the growth surface, because CNTs are electrical conductors. Therefore, we believe that the number of nucleation sites was increased by adding CNTs, and that the electroplating energy was used for nucleation rather than nuclear growth. Consequently, the crystal size of the nickel coatings decreased, and the grain boundary increased. In other words, nickel crystals became smaller, because nickel-based CNT composite coatings have a low crystal growing velocity compared with crystal nucleus generating velocity. In fact, the grain size of the nickel-based CNT composite coatings, electroplated under the conditions shown in Table 1, was almost 20 nm.

Let us turn our attention to the crystal orientation and the growth direction of nickel crystal to CNTs. Normally, the (200) nickel crystal growth direction is perpendicular to the substrates, and the columnar crystal structure formed by normal nickel electroplating. The crystal orientation of nickel was also changed because of the addition of CNTs. Because CNTs are cylindrical, the (200) nickel crystal growth direction is perpendicular to the side wall of the CNTs. As a result, the (200) plane of the nickel crystal grows in all directions and nickel-based CNT composite coatings have random crystal structures.

Table 2 shows the elastic moduli of nickel depending on the crystal orientation. These moduli were calculated by E. Kröner. The calculations indicate that the elastic modulus at the (111) plane is the highest and that at the (200) plane is the lowest. The measured elastic modulus of normal nickel coatings, which had a preferential growth of the electroplated nickel in the (200) plane direction, shown in Fig. 7, in the form of columnar structures, was 150 GPa. This value is almost the same as the calculated value of 160 GPa for the (200) plane, as shown in Table 2. The measured elastic modulus of nickel-based CNT composite coatings, which had random crystalline structures and were prepared by DC electroplating with the addition of 1.0 g/L of CNTs, was 190 GPa. This value was almost same as the calculated value (193.3 GPa) of polycrystalline nickel.
nickel, as shown in Table 2.

From the viewpoint of the rule of mixtures, the elastic modulus of polycrystalline nickel can be calculated from the percentage of an aspect of crystal orientation. Figure 7 shows the orientation index for each amount of CNTs in a plating bath. Therefore, the elastic moduli of each nickel-based CNT composite coating can be calculated from Table 2 and Fig. 7. Figure 9 shows a plot of the calculated and experimental values of elastic moduli of nickel-based CNT composite coatings against the amount of CNTs in a plating bath. The results indicate that the calculated values were almost the same as the experimental values, and the elastic modulus depended on the crystal orientation in cases of low concentration of CNTs in the matrix, such as in the case of nickel-based CNT composite coatings prepared by DC electroplating.

3.4 Effects of CNT concentration on elastic modulus

The elastic modulus of particulate-reinforced composites can be derived from the Halpin–Tsai equations:

\[
E_C = \frac{E_{Ni}\left(1 + \eta V_{CNT}\right)}{1 - q V_{CNT}} \quad (2)
\]

\[
q = \frac{E_{CNT}}{E_{Ni}} \left(1 - \frac{1}{E_{CNT} / E_{Ni} + \eta}\right) \quad (3)
\]

where \(E_C\), \(E_{Ni}\), and \(E_{CNT}\) are the elastic moduli of the composite, nickel matrix, and CNTs, respectively; \(\eta\) is an adjustable parameter; and \(V_{CNT}\) is the volume fraction of CNTs. For nickel-based CNT composites, \(E_{Ni} = 193.3\) GPa, which is calculated from the values in table 2, and \(E_{CNT} = 1200\) GPa.

Most CNTs lie on the growth surface and are embedded in nickel-based CNT composite coatings, as shown in Fig. 2; hence, the elastic modulus is calculated with \(\eta = 2\). Figure 10 shows the elastic moduli of the coatings calculated using Halpin–Tsai equations. The coatings were prepared by DC and PR electroplating under the condition that the amount of CNTs in the plating bath is 1 g/L. The volume fraction of the coating was regarded as the average of volume fraction of the coating between the surface and indentation depth, and was calculated from the results shown in Fig. 3. The measured elastic moduli of the nickel-based CNT composites formed by DC electroplating, which have a low CNT volume fraction of 6.3 vol.%, agree well with the values calculated using the Halpin–Tsai equations, as shown in Fig. 10. The difference between the measured and calculated values of normal nickel coatings was because of the change in the nickel matrix crystalline structures caused by CNTs, as is mentioned in section 3.3.

On the other hand, the measured elastic moduli of nickel-based CNT composites formed by PR electroplating, which have a high CNT volume fraction of 39.2 vol.%, were lower than those calculated using the Halpin–Tsai equation, as shown in Fig. 10. This is due to the poor dispersion of the CNTs and the existence of pores in the matrix. However, these results indicate that the elastic modulus of nickel-based CNT composite coatings increases with increasing volume fraction of CNTs in the matrix, according to the rule of mixtures.

4. CONCLUSIONS

The following conclusions were derived from the study.

1. The elastic modulus of nickel-based electroplated coatings varies depending on the CNT concentration owing to changes of the CNT composites and nickel crystal.
2. The elastic modulus of nickel-based CNT composite coatings with low concentration of CNTs can be calculated by the rule of mixtures using the percentage of an aspect of crystal orientation and the value of the elastic modulus for each crystal orientation. The calculated elastic moduli of the nickel-based CNT composite coatings were almost same as experimental values. The elastic modulus was dependent on the crystal orientation for a low concentration of CNTs in the matrix, such as in the case of the nickel-based CNT composite coatings prepared by DC electroplating.
3. The high-CNT-concentration layer can be prepared by PR electroplating. Nickel-based CNT composite coatings with a high-CNT-concentration layer at the surface have a high elastic modulus.  
4. The moduli increase with increasing CNT concentration. The measured elastic moduli agree well with the values calculated using the Halpin–Tsai equations for low CNT concentrations in the matrix. However, the measured moduli are lower than the calculated ones for high CNT concentrations.

Acknowledgments
This study was supported by Industrial Technology Research Grant Program in 2008 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References
1) Min-Feng Yu et al., "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load", Science 287 (2000) 637-640
2) Min-Feng Yu et al., "Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties", Phys Rev Lett. 84 (2000) 5552-5555.
3) Srinivasa R et al., "An analysis of the factors affecting strengthening in carbon nanotube reinforced aluminium composites", carbon 49 (2011) 533 –544
4) L. Y. Wang et al., "Friction and wear behavior of electroless Ni-based CNT composite coatings", Wear 254 (2003) 1289–1293
5) Tsunehisa Suzuki Takashi Konno, "Improvement in tool life of electroplated diamond tools by Ni-based carbon nanotube composite coatings", Precision Engineering, Volume 38, Issue 3, July 2014, Pages 659–665
6) T. Suzuki et al., "Effect of Carbon Nanotube (CNT) Size on Wear Properties of Cu-Based CNT Composite Electrodes in Electrical Discharge Machining" Journal of Solid Mechanics and Materials Engineering, (2011)
7) T. Suzuki et al., "Development of Cu-based CNT composite electrodes for low wear property in electrical discharge machining", International Journal of Electrical Machining, No.13 (2007) 41-44
8) M. I. Ismail, "Periodic reverse current electroplating and surface finishing", Journal of applied electrochemistry, Vol. 9, No. 3, 407-410 (1979)
9) Elizabeth J. Podlaha, "Selective Electrodeposition of Nanoparticulates into Metal Matrices", Nano letters, 2001, Vol. 1, No. 8, 413-416
10) Feng Wang, Susumu Arai, Morinobu Endo, "Preparation of nickel–carbon nanofiber composites by a pulse-reverse electrodeposition process", Electrochemistry Communications, Volume 7, Issue 7, July 2005, Pages 674-678
11) Chao Guo, Yu Zuo, Xuhui Zhao, Jingmao Zhao, Jinping Xiong, “The effects of pulse–reverse parameters on the properties of Ni–carbon nanotubes composite coatings”, Surface and Coatings Technology, Volume 201, Issue 24, 15 October 2007, Pages 9491-9496
12) Oliver, W.C. and Pharr, G.M., "An Improved Technique for Determining Hardness and. Elastic Moduli using Load and Displacement Sensing Indentation Experiments", Journal of Materials Research, vol. 7 (1992) 1564-1583
13) K. S. Willson et al., Tech. Proc. American Electroplaters Society, 51 (1964) 92-95.
14) Tsunehisa Suzuki, Mutsuto Kato, Takeshi Matsuda, Seiya Kobayashi, “High-temperature softening of nickel-based carbon nanotube composite coatings for the fabrication of nickel-based nanoimprint molds by thermal imprinting", Journal of Advanced Mechanical Design, Systems, and Manufacturing Vol.8, No.4, 2014, Paper No. 14-0111
15) Tsunehisa Suzuki, Mutsuto Kato, Takeshi Matsuda, and Seiya Kobayashi, "High Temperature Hardness of Electrodeposited Nickel-based Carbon Nanotube Composite Coatings", ECS transactions, 2013 50(52): 165-169
16) E. Kröner Acta Metall., 9 (1961), pp. 155–161
17) Hull D, Clyne TW. "An introduction to composite materials. 2nd ed.", Cambridge, University Press; 1996. p.66