High-temperature softening of nickel-based carbon nanotube composite coatings for the fabrication of nickel-based nanoimprint molds by thermal imprinting

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Abstract
The development of nickel mold materials that softened at high temperatures was investigated, and their use in the fabrication of replica nickel molds by thermal nanoimprinting was demonstrated. Ni-based carbon nanotube (CNT) composite coatings were formed by ultrasonic assisted electroplating using a horn sonicator. 1.6 g/L CNTs, which were 9.5 nm in diameter and 1.5 μm in average length, were added to a nickel sulfamate plating bath. The Vickers hardness of the Ni-based CNT composite coatings was over 500 HV at room temperature and under 50 HV at high temperatures over the range of 400 to 600 °C. After heat treatment at 500 °C, the grain size of the Ni-based CNT coatings became larger than that of normal Ni coatings. Ni-based CNT composite coatings had random crystals, instead of the columnar crystals in pure nickel coatings. It is thought that the softening of the Ni-based CNT composite was based on containing CNTs in grain boundaries, as well as a crystal structure transformation. To fabricate the Ni-based replica mold, a Ni-based CNT composite coating was directly imprinted at 3 MPa and 500 °C; higher than the softening temperature of the coatings. 5 μm square dot patterns from a mother silicon mold was successfully replicated by thermal nanoimprinting on the Ni-based CNT composite coating. The fabrication method of replica nickel molds was based on the high-temperature softening property of Ni-based CNT composite coatings.

Key words : Carbon nanotube (CNT), Nanoimprint, Replica mold, Composite coating, High-temperature softening, Metal matrix composites

1. Introduction
In recent years, the microfabrication of Ni-based coatings, such as nickel alloy coatings and composite coatings by electroplating and electroforming, has received considerable attention from the standpoint of applications of nanoimprint molding for optical components (Yan, et al., 2011, 2012, 2009). The electroforming method is well known for the fabrication of replica nickel molds for nanoimprinting (Hansen, et al., 2011, Heyderman, et al., 2001, Zhou and Luo, 2012). Generally, Ni-based coatings are formed on nanoimprint mother molds by electroplating and are then removed. The Ni-based coatings, which have the reverse pattern of mother mold, are used as replica nickel molds. However, electroforming is an expensive process and takes a long time for fabrication; therefore, other effective methods for easy fabrication of replica nickel nanoimprint molds are required.

The properties of Ni-based coatings have been improved and several functions have been added by alloying and adding reinforcements. Carbon nanotubes (CNTs) as reinforcements are increasingly attracting scientific and technological interest because of their unique chemical and physical properties for producing composites of metallic and non-metallic constituents. Some recent studies investigated Ni-based CNT composite coating methods by using electroless codeposition (Wang, et al., 2003) and electrocodeposition (Chen, et al., 2002) and have reported that the friction and wear properties are improved by codepositing CNTs in the matrix (Suzuki, et al., 2012). We have investigated Ni-based CNT composite coatings formed by electrocodeposition with ultrasonic agitation and have
reported that the coatings had a Vickers hardness of more than 500 HV (Suzuki and Konno, 2014). The Vickers hardness of Ni-based CNT composite coatings was almost equal to that of Ni-P coatings, which are generally used as a mold material. We have also revealed that Ni-based CNT composite coatings softened at high temperatures (Suzuki, et al., 2013a). The Vickers hardness of Ni-based CNT composite coatings was lower than that of pure nickel coatings at high temperatures over the range of 400 to 600 °C, therefore, Ni-based CNT composite coatings have the potential for use as replica nanoimprint mold materials because the mold materials should have high hardness at low temperatures for resin nanoimprints, and should also have low hardness at high temperatures for replica fabrication by nanoimprinting.

In this paper, to better understand the potential effectiveness of Ni-based CNT composite coatings for the fabrication of replica nanoimprint molds, the Vickers hardness and crystal structure of the coatings, before and after heat treatments, were investigated. The technical feasibility of the fabrication of replica nickel molds containing CNTs by nanoimprinting, which was based on high-temperature softening, was demonstrated.

2. Experimental procedures

2.1. Electroplating method and evaluation

Figure 1 shows the experimental setup of the horn sonication method (Suzuki and Kato, 2013b), with the horn sonicator immersed in the plating bath. The substrates were also immersed in the plating bath and set below the horn sonicator with the electroplating surface of the substrates facing the vibrating surface of the horn sonicator. The electroplating surface is directly vibrated by the intense ultrasonic wave from the horn sonicator as it travels through the solution. Cavitation occurred as a result of the intense ultrasonic wave near the substrate surface. The distance between the vibrating surface and the substrates was about 10 mm. The diameter of the vibrating surface was 22 mm. The sonicator horns were driven by connecting a bolt-clamped Langevin transducer (BLT), which had a resonant frequency of 27 kHz. The transducer was driven by a 200 W electrical input.

Table 1 lists the plating bath composition and operation conditions for producing Ni-based CNT composite coatings. The coatings were deposited on high-speed steel plate substrates by electroplating using a nickel sulfamate plating bath, adding 0–10 g/l of CNTs with anionic surfactants under galvanostatic conditions. CNTs used in this study

<table>
<thead>
<tr>
<th>Bath</th>
<th>Ni(NH$_2$SO$_3$)$_2$ · 4H$_2$O: 500 g/L, NiCl$_2$·6H$_2$O: 4 g/L, H$_3$BO$_3$: 33 g/L, CNTs: 0 – 10 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agitation</td>
<td>Horn sonication</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>45 °C</td>
</tr>
<tr>
<td>Current density</td>
<td>–5 A/dm$^2$</td>
</tr>
<tr>
<td>Process time</td>
<td>60 min</td>
</tr>
<tr>
<td>Substrate</td>
<td>High Speed Steel (SKH51)</td>
</tr>
</tbody>
</table>

![Table 1 The electroplating bath composition and the operating conditions](image)

![Fig. 1 Schematic illustration of the ultrasonic-assisted electroplating setup using a horn sonication method.](image)

![Fig. 2 Replication procedure of Ni-based CNT composite mold by nanoimprinting. (a) A Ni-based CNT composite coating is prepared. (b) High-temperature softening allows the coating to faithfully reproduce the mother mold. (c) Upon cooling, the coating retains the mother mold impression.](image)
were multi-walled carbon nanotubes (Nanocyl S.A., NC7000) and were typically 9.5 nm in diameter and 1.5 μm in length. The substrates were used as anodes. Pure Ni was used as the cathode. The plating bath was controlled at 45 °C. The current density was controlled at 5 A/dm² by a galvanostat.

The Vickers hardness of the Ni-based CNT composite coatings was measured using a micro-Vickers hardness tester (Akashi, HM-124, Load: 0.49 N) before and after heat treatment at 100 – 600 °C. The crystal structures of the coatings were analyzed by electron backscatter diffraction (EBSD) and X-ray diffraction (XRD). The high-temperature hardness of the coatings was measured over the temperature range from room temperature to 600 °C by a high-temperature hardness tester (NIKON, QM-2, Load: 0.98 N).

2.2 Replication method

Figure 2 shows the nanoimprinting replication procedures of a Ni-based CNT composite mold. Ni-based CNT composite coatings on the substrates were formed by electroplating and replicated by thermal nanoimprinting using a nanoimprint lithography apparatus (SCIVAX, X-300) with silicon mother molds with 5 μm square dot patterns. The process temperature was 500 °C, pressure was 3 MPa, and holding time was 60 sec.

3. Results and discussion

3.1. Effects of heat treatment on room-temperature hardness and crystal structure of Ni matrix

Figure 3(a) show an SEM image of the surface of the Ni-based CNT composite coatings formed by electroplating using the horn sonication method. There were no nodules on the surface. The surface roughness of the coating was 0.1 μm Ra.

Figure 3(b) shows an SEM image of CNTs in a Ni-based CNT composite coating etched by acid after electroplating. Well-dispersed CNTs in the nickel matrix could be observed.

Figure 4 plots the room-temperature Vickers hardness of the coatings after heat treatment at the specified temperatures. The Vickers hardness of the Ni-based CNT composite coatings were about 2.5 times higher than that of normal nickel coatings. For heat-treatment temperatures up to 300 °C, the hardness of the composite coatings steadily decreases with increasing the temperature and drops down to 150 HV. Increasing the amount of CNTs beyond...
300 °C resulted in a slower decrease in hardness. Over the temperature range of 200 to 600 °C, the Vickers hardness of Ni-based CNT composite coatings was same as that of pure nickel coatings after heat treatment. The hardness trend was not dependent on the amount of CNTs in the plating bath.

Figures 5 and 6 show the EBSD inverse pole figures (IPFs) and pole figure of cross-sectional Ni-based coatings with or without 1.6 g/l CNTs after heat treatment at 500 °C for 3 h. The grain size of the Ni-based CNT composite coatings was larger than that of normal Ni coatings. The crystal structure of normal Ni coatings had a preferred crystal orientation, shown in Fig. 6(a). The crystal structure of Ni-based CNT composite coatings had no preferred crystal orientation, shown in Fig. 6(b).

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Figure 7 plots the XRD orientation index of the surface of Ni-based coatings before and after heat treatment (temperature: 500°C, time: 3 h). An orientation index of 1 indicates a random crystal structure. Normal Ni coatings had columnar crystal structures. Ni-based CNT composite coatings had a random crystal orientation with or without heat treatments.

3.2. Mechanism of the changes in Ni matrix crystal structure by the addition of CNTs

In the case of normal nickel electroplating without additives using the conditions shown in Table 1, XRD analysis indicated the presence of preferential growth of the electroplated nickel in the (200) plane direction, shown in Fig. 7(a), manifesting as 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 changed, shown in Fig. 7(b). Figure 8 shows an SEM image of the CNTs at the growth surface of nickel, and nickel nucleation on the CNTs can be observed. CNTs immediately become nickel nucleation sites after the CNTs touch the growth surface because CNTs are electrical conductors. Therefore, we believe that nucleation sites were increased by adding CNTs, and that the electroplating energy was distributed to nucleation more than nuclear growth. Consequently, the crystal size of the Ni coatings decreased, and the grain boundary increased. In other words, nickel crystals became small because Ni-CNT has the crystallization characteristic of a low crystal growing velocity compared with the crystal nucleus generating velocity. In fact, the grain size of the Ni-CNT composite coatings, electroplated under the conditions shown in Table 1, was almost 20 nm (Suzuki, et al., 2013a).

In addition, the crystal orientation of nickel was also changed by the CNTs. Figure 9 shows the schematic images of nickel crystal nucleation and growth on CNTs. CNTs are cylindrical, so 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 up in all directions and Ni-based CNT composite coatings have random crystal structures.

3.3. Mechanism of the changes on crystal structure by heat treatments

After heat treatment, the grain size of the Ni-based CNT composite coatings was bigger than that of normal nickel coatings. We believe that the grain size difference between Ni-CNT and Ni occurred as a result of the difference in deposition crystal structure and the difference in misfit dislocation density.

As-deposited Ni-based CNT composite coatings consist of small and randomly distributed crystals. Therefore, there is a very high chance that grains sharing a boundary have a similar crystal structure. As a result, the recrystallization energy of Ni-based CNT composite coatings might be lower than that of normal nickel coatings.

The misfit dislocation density of Ni-based CNT composite coatings must be much higher than that of normal as-deposited nickel coatings, because there are a lot of misfit dislocations at the boundaries between CNTs and nickel.
grains. The misfit dislocation is the energy of recrystallization. Therefore, we believe that high misfit dislocation density could drive recrystallization and create large grains in the Ni-based CNT composite coatings after heat treatment.

Figure 10 shows thermogravimetric (TG) and differential thermal analysis (DTA) of Ni-based coatings with/without CNTs before/after heat treatment at 500 °C. Thermal analysis indicated that an exothermic reaction occurred in the as-deposited coatings between 350 to 400 °C, and that the calorific values of Ni-based CNT composite coatings were much higher than that of normal nickel coatings. The exothermic reaction did not occur in Ni-based CNT composite coatings after heat treatment. The exothermic reaction was irreversible. Thus, the exothermic reaction indicates the recrystallization of the nickel coating. High calorific values indicate the ability to undergo large recrystallizations. These results support our beliefs about the creation of large grains in Ni-based CNT composite coatings by heat treatment.

3.4. High-temperature softening of Ni-based CNT composite coatings

Figure 11 plots the high-temperature hardness of normal electrodeposited nickel coatings and Ni-based CNT composite coatings. The hardness of both nickel coatings decreased with increasing temperature. The rate of decrease in the hardness of the Ni-based CNT composite coatings was greater than that of normal nickel coatings. The hardness of Ni-based CNT composite coatings at room temperature was three times higher than that of normal coatings. However, the hardness of the composite coatings at temperatures over 300 °C was lower than that of normal coatings,

Fig. 10 Thermogravimetric (TG) and differential thermal analysis (DTA) of Ni-based coatings with/without CNTs before/after heat treatment at 500 °C.

(a) Normal Ni as deposited
(b) Ni-CNT, as deposited, showing a recrystallization event at 377°C

(c) Ni-CNT after heat treatment. No further recrystallization is evident.
and decreased to under 50 HV, indicating that Ni-based CNT composites have the property of high-temperature softening at 400 – 600 °C, much like a superplastic material. It is thought that the high-temperature softening of Ni-based CNT composite coatings can be attributed to misfit dislocations between the CNTs and the Ni matrix, and to the random crystal structure of the Ni matrix. The high-temperature softening might be induced by structural superplasticity with grain growth.

3.5. Fabrication of nickel-based nanoimprint molds by thermal nanoimprinting

Figure 12 show SEM images of replica nickel molds containing CNTs formed by thermal nanoimprinting (process temperature: 500 °C, pressure: 3 MPa, time: 60 sec). We can see the 5 μm square dot patterns, which were replicated by

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nanoimprinting on a Ni-based CNT composite coating. The results indicate the technical feasibility of the fabrication of replica nickel molds containing CNTs by nanoimprinting, based on high-temperature softening. Figure 13 show SEM images of replica nickel molds formed by thermal nanoimprinting (process temperature: 500 °C, pressure: 3 MPa, time: 60 sec). As opposed to the nickel molds containing CNTs, there were few dot patterns in the normal Ni-coating. The pattern shape was not uniform

4. Conclusions
Fabrication of replica nickel molds by thermal nanoimprinting and the development of nickel mold materials, which softened at high temperatures, were investigated. The Vickers hardness of Ni-based coatings was improved, by codepositing CNTs as reinforcements in the nickel matrix, to over 500 HV at room temperature. Ni-based CNT composite coatings had random crystals, instead of the columnar crystals in pure nickel coatings.

The room-temperature Vickers hardness of the Ni-based CNT composite coatings decreased with increasing heat-treatment temperature, and shows the same Vickers hardness as pure nickel coatings at a heat-treatment range of 200 to 600 °C. After heat treatment at 500 °C, the grain size of the Ni-based CNT coatings became larger than that of normal coatings by recrystallization. An exothermic reaction occurred in the Ni-based coatings during deposition between 350 to 400 °C, and the calorific values of the Ni-CNT coatings were much higher than that of normal nickel coatings. The exothermic reaction was irreversible and was related to the recrystallization of the Ni matrix. The high calorific values of Ni-based CNT composite coatings indicate the high energy required for the recrystallization.

The high-temperature Vickers hardness of the Ni-based CNT composite coatings also decreases with increasing temperature, and was about 50 HV at temperatures in the range of 400 to 600 °C; lower than that of normal coatings. Ni-based CNT composite were able to be softened at high temperatures due to the CNTs, which induced a lot of misfit dislocations, and by the crystal structures, which had random and small grains. Replica nickel molds containing CNTs with 5μm square dot patterns could be fabricated by thermal nanoimprinting using the high-temperature softening of Ni-based CNT composite coatings.

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