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# Evaluation of Friction Coefficient and Adhesion Properties of Silicon Carbon Nitride Films Prepared by HWCVD

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We have investigated the friction-coefficient properties of silicon carbon nitride (SiCN) films deposited on stainless steel substrates and the adhesion properties of SiCN films deposited on Si(100). The SiCN films were deposited by hot-wire chemical vapor deposition using hexamethyldisilazane and ammonium. It was found that SiCN coating was able to effectively reduce the frictional coefficient of the stainless steel substrates. The adhesion strength was measured by surface-interface physical property analysis equipment (SAICAS) and was found to be 45 N/m for the as-deposited SiCN film on Si(100). Furthermore, a maximum adhesive strength of 92 N/m was obtained after treating the film for 10 min at 1000 °C.

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## 1. Introduction

Surface coating is crucial for improving the performance and prolonging the lifetime of metal products, such as molds and cutting tools. Diamond-like carbon (DLC) is a promising candidate for use as coating material. DLC is a metastable amorphous carbon with excellent tribological and mechanical properties [1] that make it well suited for the hot embossing process. However, high internal stress, poor adhesion to substrates, and limited coating thickness have prevented the use of DLC in certain applications [2, 3]. In addition, the beginning of graphitization (i.e., $sp^3$ to $sp^2$ transformation) at high temperatures [4] renders DLC unsuitable for coating molds under elevated temperature conditions. We believe that silicon carbon nitride (SiCN) films offer a solution to these problems. SiCN films are transparent, insulating, and have high hardness, frictional tolerance, as well as weather resistance. Hot-wire chemical vapor deposition (HWCVD), sometimes referred to as Cat-CVD, has attracted attention as a possible alternative to plasma-enhanced CVD for low-temperature film deposition [5–7]. Moreover, $SiH_4$ is typically required for the deposition of SiCN films, but general industries are not allowed to use $SiH_4$ owing to its volatile and poisonous nature. To avoid these safety issues, we have previously deposited SiCN films by HWCVD, using non-explosive organic liquid hexamethyldisilazane (HMDS) [8], which has allowed the use of SiCN films by general industries.

We will determine whether SiCN can be applied as a coating film for metal products, especially for molds. As an introductory study, we have investigated the friction-coefficient properties of SiCN films deposited on stainless steel (SUS) substrates and the adhesion properties of SiCN films deposited on Si(100). We have also investigated the adhesion properties of post-heat-treated SiCN films on Si(100).

## 2. Experimental

Figure 1 shows the schematic cross-section of the HWCVD apparatus. Prior to deposition Si(100) substrates were treated in HF solution. Then, Si(100) and/or mirror-polished SUS 304 substrates were placed in a vacuum chamber maintained at a pressure of $1.5\times10^{-4}$ Pa, and an $NH_3$ radical treatment was performed for 10 min. HMDS was subsequently supplied to the chamber and a SiCN film was deposited under the typical deposition conditions shown in Table I. We have placed a 0.5 mm diameter zigzag-shaped tungsten (W) filament below the substrate. This filament and the substrate were maintained at temperatures of 1600 °C and 250 °C, respectively. HMDS and $NH_3$ become active radicals by the catalytic cracking reaction on the heated W wire, similar to other kind of films growth, which are using HWCVD [9]. Then the produced radicals react on the substrate and contri-

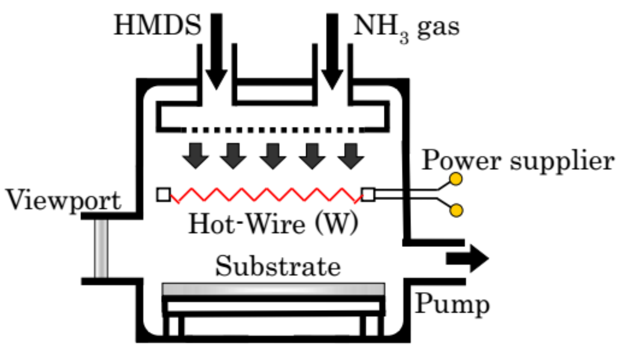


Fig. 1. Schematic diagram of the HWCVD.

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bute to growth of SiCN films on the substrate. The substrate temperature was monitored using a thermocouple attached to the substrate holder. In addition, the film thickness and refractive index were measured by ellipsometry using a 632.8 nm wavelength He-Ne laser.

TABLE I
Exprimental conditions.

| | |
|---|---|
| Substrates | Si(100), SUS304 |
| Catalyst material | Tungsten(W) |
| Back pressure [Pa] | $1.5 \times 10^{-4}$ |
| Catalyzer temperature [°C] | 1600 |
| $NH_3$ gas flow rate [sccm] | 50 |
| $NH_3$ treatment [min] | 10 |
| Gas pressure [Pa] | 1.2 |
| HMDS gas flow rate [sccm] | 1.3 |

The friction coefficient of the SiCN film deposited on SUS 304 was measured using an apparatus in accordance with the Japanese Industrial Standard (JIS) K 7125. The measurement set-up is shown in Fig. 2. The measurement conditions were as follows, loading weight of 5 kN and test speeds of 10 mm/min, 50 mm/min, and 100 mm/min. The contact area of the sample was $100 \times 100$ mm$^2$. A mirror-polished SUS 304 substrate was coated with a SiCN film with a thickness of about 280 nm.

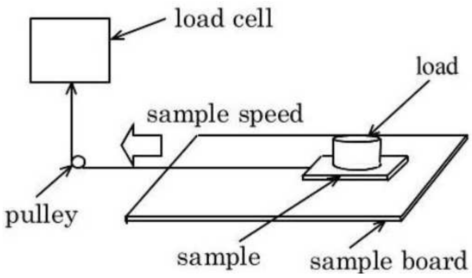


Fig. 2. Schematic diagram of the friction coefficient set-up, in accordance with the Japanese Industrial Standard (JIS) K 7125.

The adhesion strength and film structure of a SiCN film with a thickness of about 100 nm deposited on Si(100) were measured by surface-interface physical property analysis equipment (DAIPLA WINTES Corp., SAICAS BN-1) [10, 11] and determined using Fourier transform infrared (FTIR) spectroscopy, respectively.

Furthermore, the films deposited on Si(100) were heat-treated for 10 min in nitrogen ($N_2$) at temperatures ranging from 400 °C to 1000 °C. Heat treatments in nitrogen were also performed at a fixed temperature of 1000 °C for periods of time ranging from 10 to 240 min.

## 3. Results and discussion

Figure 3 shows the relation between the frictional force and the sliding distance for the SUS 304 substrates with and without SiCN film deposition. It is found that the frictional force is drastically reduced for the sample with the SiCN coating, compared to the uncoated sample.

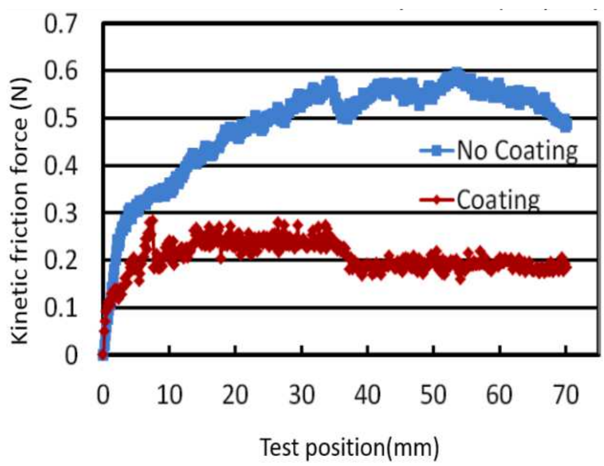


Fig. 3. Frictional force vs. sliding distance for the SUS 304 substrates with and without SiCN film deposition.

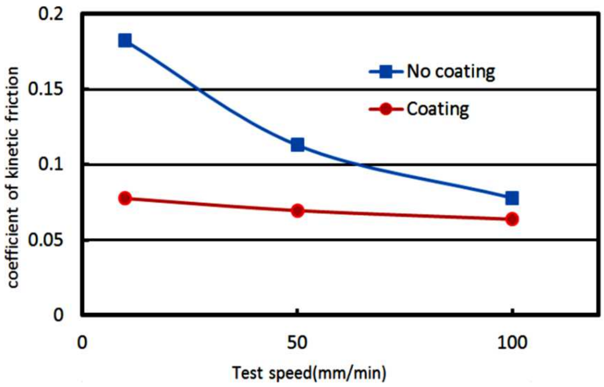


Fig. 4. Dynamic friction coefficient vs. sample velocity.

Figure 4 depicts the relationship between the dynamic friction coefficient and sample velocity. The coefficient of dynamic friction was calculated by dividing the mean value of the frictional force by the load at the slip distance of 10 mm or more, and the sliding distance of 60 mm. It was revealed that the change in the dynamic friction coefficient of the SiCN-coated sample is smaller than that of the uncoated sample. It was also found that the dynamic friction coefficient is reduced when the test speed is higher.

It is concluded that SiCN coating is able to effectively reduce the frictional coefficient of the SUS substrate.

Figure 5 shows the composition ratios of the SiCN films on Si(100), obtained by FTIR spectroscopy. Heat treatment resulted in a decrease in the fraction of Si–C bonds from $\sim 60\%$ in the as-deposited film to $\sim 20\%$ after heating at 1000 °C. Additionally, the fraction of Si–O bonds has increased with the heat treatment and has saturated above 700 °C. The SiCN surface is believed to be oxidized by the heat treatment.

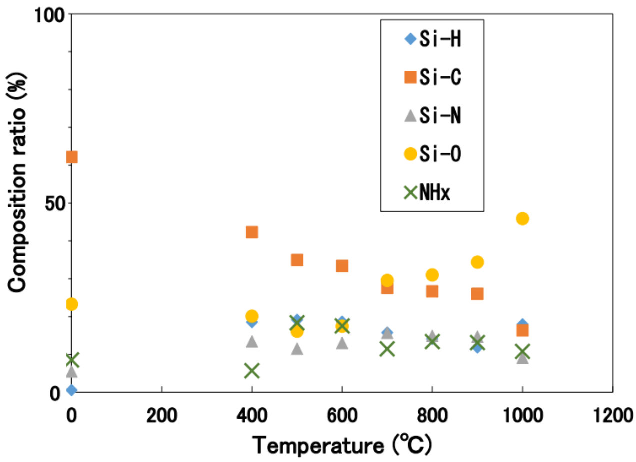


Fig. 5. Composition ratio of SiCN vs. heat treatment temperature (treatment time was fixed at 10 min).

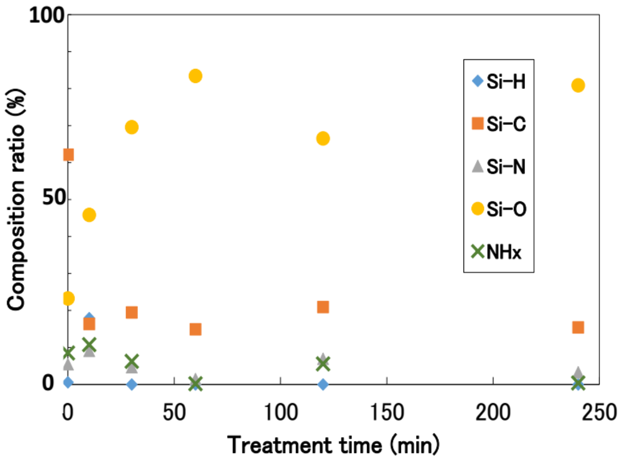


Fig. 6. Composition ratio of SiCN vs. heat treatment time (temperature was fixed at 1000 °C).

Figure 6 shows the relation between the composition ratio of SiCN and heat-treatment time. The temperature was fixed at 1000 °C. It was revealed that Si–C and Si–O bond ratios decrease and increase from 23 to $\sim$ 80%, respectively, with increasing heating time. The fraction of Si–O bonds has saturated after 60 min, indicating that the oxidization limit of the SiCN film surface had been reached.

Figure 7 shows the relation between the adhesion force of SiCN/Si(100) and heat-treatment temperature. The treatment temperature was fixed at 10 min. It was found that the adhesion strength increases, in general, with increasing heat-treatment temperature. For example, the adhesion strength has increased from 45 N/m in the non-heat-treated sample and saturated at $\sim$ 93 N/m after heat treatment at temperatures of 800 °C and higher.

Figure 8 shows the relation between the adhesion force of SiCN/Si(100) and heat-treatment time. The temperature was fixed at 1000 °C. It was found that the adhesion strength increases from 49 to 90 N/m for heat-treatment time of up to 10 min, and decreases thereafter.

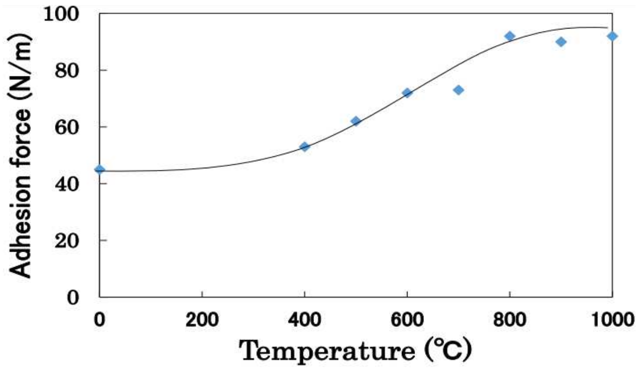


Fig. 7. Adhesion force of SiCN/Si(100) vs. heat treatment temperature (treatment time was fixed at 10 min).

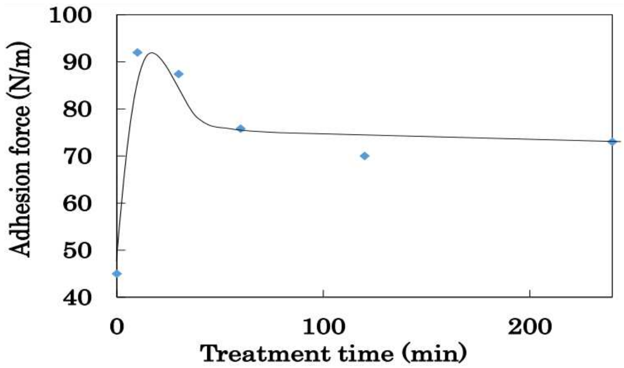


Fig. 8. Adhesion force of SiCN/Si(100) vs. heat treatment time (temperature was fixed at 1000 °C).

The adhesion strength of a 200 nm thermal $SiO_2$ film deposited on a Si(100) substrate was measured by SAICAS and found to be 49 N/m. Therefore, the adhesion strength of SiCN deposited on Si(100) by HWCVD is much higher than that of thermal $SiO_2$. The adhesion strength increases with heat treatment, which possibly stems from an improvement in the film density and increased fraction of Si–O bonds. However, at heat-treatment temperatures above 800 °C, the adhesion strength did not increase significantly with the increasing number of Si–O bonds. Therefore, it is believed that increasing fractions of Si–O bonds does not influence the adhesion strength. Detailed investigations of the density and bonding states of the SiCN films are necessary to identify the mechanism that leads to increased adhesion strength with heat treatment.

## 4. Conclusions

In this work we have investigated the friction-coefficient properties of SiCN films deposited on SUS substrates, and the adhesion properties of SiCN films deposited on Si(100) by HWCVD. It was found that the SiCN coating was able to effectively reduce the frictional coefficient of the SUS substrates. The adhesion strength was measured by SAICAS and found to be 45 N/m for the as-deposited SiCN film. Furthermore, a maximum adhesive strength of 92 N/m was obtained after heat-treating the film for 10 min at 1000 °C.

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