DIAMOND DEPOSITION BY MEANS OF TANTALUM FILAMENT ON WC-Co ALLOY AND OTHER HARD MATERIALS

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Some diamond deposition experiments on WC-Co alloy and other hard materials by the thermal CVD method were performed by using Ta filaments with varying filament temperature \( (T_f) \). The deposition behavior and adhesion strength of the diamond film were investigated. At a lower \( T_f \) of 2000°C, scratching and etching of the substrate surfaces were necessary for diamond film formation on the WC-Co substrate, but at a higher \( T_f \) of 2600°C the deposition density and rate markedly increased and diamond films were obtained without any surface treatment. The film deposited on the Si₃N₄ substrate was excellent in resistance to flaking due to thermal stress compared with the films on the WC-Co, Ti(C,N)–Mo₂C–Ni and Al₂O₃ substrates.

1. Introduction

The thermal CVD (hot-filament) method\(^1,2\) is an important process for diamond deposition under low pressures and is expected to be applied in many industrial fields. Diamond film coating on hard materials is one of the most significant applications of this method. Recently, we have used a Ta(TaC) filament\(^3\) in this method instead of the W(WC) filament used in previous studies\(^4,5,6\). The use of a Ta(TaC) filament enables us to increase the filament temperature \( (T_f) \) from 2000°C to about 3000°C, since TaC has a very high melting point (about 4000°C) compared with WC (about 2800°C). At high \( T_f \), improvements in the deposition rate and density would be expected. In this report, using a Ta filament in the thermal CVD method, the deposition behavior mainly on WC–Co is examined in relation to \( T_f \) and the substrate surface conditions. The adhesion of diamond films deposited on WC–Co, Ti(C, N)–Mo₂C–Ni, Al₂O₃ and Si₃N₄ is also examined.

2. Experimental

Figure 1 shows a schematic view of the diamond deposition apparatus. Commercial Ta wire with Ø0.5 mm was used for the filaments. Before the deposition experiments, the Ta filament was carburized at 2400°C in H₂–5%CH₄ gas until it changed to TaC. The conditions for diamond deposition are listed in Table I. The substrates used for deposition are WC–Co, Ti(C, N)–Mo₂C–Ni, Al₂O₃ and Si₃N₄. Surface conditions of the WC–Co substrate were varied in the following four ways: (a) as polished, (2) etched in HNO₃ to remove the Co phase, (3) scratched by diamond powder, (4) scratched and then etched. The surface

conditions of the other substrates were as-polished. The deposits on the substrates were examined by optical and scanning electron microscopy and Raman spectroscopy. The residual stresses of the diamond films on the substrates were also examined by means of the 2θ−sin²θ method.

3. Results and discussions

Figure 2 shows the surface structures of deposits on WC–Co substrates with various surface conditions after deposition at \( T_i \) 2000°C for 30 min in \( \text{H}_2-1\%\text{CH}_4 \). The density of the deposited particles is influenced by the substrate surface condition; both etching and scratching treatments improve the density, and the density is highest on the surface scratched and then etched. On the Co phase of the non-etched substrates of (a) and (c), other deposits of fine particles are observed. The Raman spectra of the whole of the deposits indicated that, though the deposits on the etched substrates of (b) and (d) consisted exclusively of diamond, the deposits on the non-etched substrates of (a) and (c) were mixtures of diamond and graphitic carbon. Thus, the fine particles on the Co phase were regarded as graphitic carbon. At this \( T_i \), almost exclusively graphitic carbon formed at \( \text{CH}_4 \) concentration higher than 1%, irrespective of substrate surface conditions.

Figure 3 shows the surface structures of deposits on WC–Co substrates after deposition at 2600°C for 10 min in \( \text{H}_2-3\%\text{CH}_4 \). The density and deposition rate are markedly improved compared with the results at 2000°C; film deposits form on all surfaces. The Raman spectra showed that almost exclusively diamond formed on all surfaces. Moreover, at this \( T_i \), it was possible to deposit diamond films at higher \( \text{CH}_4 \) concentrations (less than 6%) than at \( T_i \) of 2000°C. This result may be closely related to the fact that the increase of \( T_i \) enhances the formation of atomic hydrogen, which has been said to play an important role in diamond deposition\(^{1,23}\).

Figure 4 shows the surface structures of deposits on as-polished WC–Co substrate after deposition for short times (1 or 3 min) at 2600°C in \( \text{H}_2-3\%\text{CH}_4 \). After 1 min, crystalline particles near the corners of the WC phase and fine deposits on the Co phase are observed, but after 3 min, the fine deposits are scarcely observable. The Raman speci-

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Table 1. Deposition conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Values</th>
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<tbody>
<tr>
<td>Gas composition</td>
<td>( \text{H}_2-(1-10)%\text{CH}_4 )</td>
</tr>
<tr>
<td>Total gas pressure</td>
<td>4 kPa</td>
</tr>
<tr>
<td>Total gas flow rate</td>
<td>20 ml/min</td>
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<tr>
<td>Filament temperature</td>
<td>2000–2600°C</td>
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<tr>
<td>Substrate temperature</td>
<td>900°C</td>
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<tr>
<td>Distance between filament and substrate</td>
<td>5 mm</td>
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</table>
tria in relation to deposition time are shown in Fig. 5. Although in the spectrum of 1 min a broad peak near 1550 cm\(^{-1}\) due to graphitic carbon appears as well as a sharp peak at 1334 cm\(^{-1}\) due to diamond, the broad peak's height decreases with increasing deposition time. This fact indicates that the graphitic carbon content in deposited films decreases with increasing deposition time.

A model of deposition behavior at high \(T_i\) is shown in Fig. 6. In the first stage, diamond particles precipitate mainly on the corners of WC grains and graphitic carbon particles form on the Co phase. In the second stage, diamond particles not only precipitate on the faces of WC grains, but diamond particles which have formed on the corners of WC grains start growing to cover the deposited graphitic carbon, or diamond particles precipitate on graphitic carbon. Such effects are caused by the high deposition rate at high \(T_i\). In the third stage, diamond films grow over the whole substrate surface.

Figure 7 shows the surface structures after deposition at 2600°C in H\(_2\)-3%CH\(_4\) on Si\(_3\)N\(_4\), Ti(C, N)-Mo\(_2\)C-Ni and Al\(_2\)O\(_3\) with as-polished surfaces. Figure 7 and the Raman spectra of deposits on these substrates indicated that diamond films were deposited on all substrates.

Figure 8 shows the appearances of diamond films of about 5 \(\mu\)m in thickness on the four substrates. In this figure, diamond films look dark gray. On the Ti(C, N)-Mo\(_2\)C-Ni and Al\(_2\)O\(_3\) substrates, flaking of films is observed. Figure 9 shows the appearances of diamond films about 10 \(\mu\)m in thickness on Si\(_3\)N\(_4\) and WC-Co substrates. The film on WC-Co has partly flaked off. Since film flaking always occurred during cooling after depo-
Fig. 8. Appearance on optical micrographs of diamond films about 5 μm in thickness. (a) Si₃N₄, (b) WC–Co, (c) Ti(C, N)–Mo₅C–Ni, (d) Al₂O₃.

Fig. 9. Appearance of diamond films about 10 μm in thickness. (a) Si₃N₄, (b) WC–Co.

sition, it is attributed to thermal stress arising from the difference in contraction during cooling between the diamond films and the substrates.

The thermal expansion coefficients of diamond, Si₃N₄, WC, TiC and Al₂O₃ are 3.0, 3.3, 4.0, 8.0 and 8.0 (×10⁻⁶ K⁻¹)⁷,⁸, respectively. The substrate thickness (2 mm) is so much greater than the thickness of diamond films (≤10 μm) that the amount of thermal stress (σ) in diamond films can be approximated by the following equation; \( \sigma = (\rho_{\text{dia}} - \rho_{\text{sub}}) \times \Delta T \times E_{\text{dia}} \). Here, \( \rho_{\text{dia}} \) and \( \rho_{\text{sub}} \) are the thermal expansion coefficients of diamond and substrates, respectively; \( \Delta T \) is the difference between substrate temperature (900°C) at deposition and room temperature; \( E_{\text{dia}} \) is Young’s modulus of diamond (1 TPa)⁷. The calculated value of σ for the films on WC–Co substrate is about −0.9 GPa (compression). On the other hand, residual stresses in the diamond films were measured by means of the 2θ–sin²θ method, where CuKα and the (311) peak were used, and values of \( \theta_0 \) and Poisson’s ratio of diamond were 50.3° and 0.27, respectively. The measured value of stress in films 5 μm in thickness deposited on a WC–Co substrate was about −0.9 GPa, which agreed with the calculated value. The stress in films on the Si₃N₄ substrate, which was estimated at about −0.3 GPa by calculation, was so small that it was not possible to be exactly measured.

When the diamond deposition on hard materials is intended to be applied to cutting tools and wear-resistant materials, the weak adhesion between diamond films and substrates is the most important problem to be solved. This study revealed that Si₃N₄ was superior to WC–Co in resistance to flaking by thermal stresses. While Si₃N₄ substrate seems to be suitable for diamond coating, the adhesion between diamond films and hard material substrates must be studied in more detail.

4. Conclusion

Using Ta(TaC) as a filament in the thermal CVD of diamond and WC–Co and other hard material substrates, the behavior of diamond deposition and diamond film adhesion were examined. The results obtained are as follows:

(1) In the deposition at a lower \( T_1 \) of 2000°C, the density of diamond particles deposited on a WC–Co substrate was markedly affected by substrate surface treatments; scratching and etching treatments of substrate surfaces were necessary for diamond film formation.

(2) In the deposition at a higher \( T_2 \) of 2600°C, however, the deposition density and rate became so high that diamond films were obtained without any surface treatment.

(3) The film deposited on substrates tended to flake during cooling after deposition due to thermal stress. The value of the stress in the film on the WC–Co substrate was about −0.9 GPa.

(4) The films on Ti(C, N)–Mo₅C–Ni and Al₂O₃ substrates flaked much more easily than the film on WC–Co, and the film on Si₃N₄ substrate flaked least easily.

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