Article

Application of Micro Slurry-Jet Erosion (MSE) for the Evaluation of Surface Properties of PVD TiN / TiCN Two-Layer Coatings

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In this study, the potential of a Micro Slurry-jet Erosion (MSE) test to swiftly evaluate the intrinsic surface strength properties of thin multi-layer coatings is demonstrated. A slurry containing 1.2 μm alumina particles was impacted at high velocity perpendicular to PVD TiN/TiCN (TiCN on top of TiN) and TiN coatings deposited on high-speed steel by a hollow cathode discharge (HCD) or an cathodic arc (CA) method. In addition, nano-indentation and XRD, GDOES analyses were done for the original surfaces. By measuring the variation of erosion depth against test time, the MSE test made it possible to evaluate the individual erosion properties of TiCN and TiN layers independent of the substrate. Although the hardness of TiCN layers, coated by HCD or CA, was measured with nano-indentation and found to be approximately 20% higher than for TiN, the erosion rates of TiCN layers were found to be between 32% and 38% of the erosion rate of TiN. For the HCD coating, the erosion proceeded uniformly and produced a mostly smooth surface. On the other hand, for the CA coating, a pitted surface was observed. The existence of the hollows blemishes which caused by macroparticles i. e. droplets in the coating may affect the difference in the erosion rates between HCD and CA coatings. Consequently, the MSE test may be useful to evaluate the difference of the morphology of coatings as well as the surface strength which are related with the fabrication process.

Keywords: micro slurry-jet erosion, MSE, surface strength evaluation, two-layer coating, TiN/TiCN

1. Introduction

Various thin monolayer and multilayer coatings are being rapidly investigated and eventually used in practice for tools used for metal cutting and forming [1,2].

Particularly TiCN coatings have properties of high hardness and low friction, which are typical properties of TiC coatings, together with the high toughness associated with TiN coatings [3]. For the deposition of TiCN coating, chemical vapor deposition (CVD) processes are widely used in industry. However, the CVD process requires relatively high temperatures (about 1000°C) at which diffusion and chemical reactions are activated, resulting in the change of size of coated tools and components. These behaviors become serious problems for industrial application of TiCN coating to precision dies or tools, so that the TiCN coating by CVD generally changes to the TiCN coating by physical vapor deposition (PVD) which is operated at low temperature, i. e. 300 to 450°C in the fabrication. When the TiCN coating with high carbon content is deposited, the toughness decreases remarkably, and also adhesive property against substrate materials and impact fracture resistance become worse. Thus a two-layer coating is fabricated in such a way that the carbon content changes gradually or stepwise along the depth in the layer.

The fundamental properties of two-layer coating are normally evaluated by nano hardness test and scratch test. In addition, friction and wear tests and also tool service life test are used [4-7]. However, most of these tests cannot evaluate the properties of the coating, the substrate and the individual interfaces independently. We proposed a new type of solid particle impact test and applied it to the evaluation of the various thin hard coatings and CVD TiC/TiN two-layer coatings [8,9]. From a series of research of MSE evaluation, we found
that the MSE test has very good properties to evaluate hard coatings. Furthermore, it is necessary to expand the experience of MSE-based evaluation to various coatings, such as single and/or two-layer TiCN coatings. In addition, if the MSE test is to be applied on a commercial scale to commercial coatings, the strong points and weak points of the MSE test must be known.

In this study, our developed Micro Slurry-jet Erosion (MSE) test was used to evaluate the surface strength properties of two-layer PVD coating. The relation of the MSE test results and the surface properties of the tested coating were clarified. Based on the findings obtained here, the merits and the future development of the MSE evaluation method are also discussed.

2. Experimental methods

2.1. Test apparatus and procedure

Figure 1 shows a schematic view of the test apparatus. It consists of a specimen holder, a tank and a stirrer to mix solid particles in liquid, a nozzle to eject the slurry-jet, a regulator to adjust compressed air pressure and a solenoid valve connected with a timer to control on-off of the slurry-jet flow.

A flowing stream of water containing solid particles pumped from the tank is mixed with compressed air in the nozzle, and eventually the slurry-jet is ejected at high velocity into the atmosphere. The slurry-jet velocity is regulated by the pressure (0 to 0.5 MPa) of the compressed air. For the pressure of 0.5 MPa used in this experiment, the maximum velocity was estimated to be approximately 100 m/s at the exit of the nozzle using a high-speed video camera to observe the ejected slurry-jet [10]. The cross-section of the nozzle is square, 3 × 3 mm², which generates a square scar on a flat specimen.

The angle of the slurry-jet relative to the test surface was set at 90 degrees. The test piece was mounted at 10 mm distance from the end of the nozzle. The test liquid was pure water containing angular alumina particles with an average diameter of 1.2 μm, see Fig. 2. The hardness of the alumina particles are estimated to range from HV = 1800 to 2000 [11]. The erodent, i.e., angular alumina particles, was added in a concentration of 3 mass% into pure water, and the slurry was kept at room temperature. For each test, 2 liters of slurry was used.

The geometry of the eroded surface was measured with a stylus profilometer along the centerline of the square erosion scar to obtain the erosion loss of the coatings after each test. The central region of the square erosion scar is uniformly eroded and shows almost uniform depth.

2.2. Materials

Two kinds of specimens of commercial coatings, which were fabricated by two different techniques by different coating companies, were used in this study. One was PVD coated by a hollow cathode discharge (HCD), designated HCD coating in this paper, and the other was coated by cathodic arc (CA), designated CA coating. For the TiN/TiCN coating, the deposition sequence started with the deposition of a TiN layer followed by the TiCN layer. Table 1 summarizes the deposition system, substrate materials, thickness (measured with a calotest) and mechanical properties.

For the HCD coating, the substrate was vacuum tempered and quenched high-speed steel (SKH51), whose Vickers hardness was 820 ±10. For the CA coating, the substrate was powder metallurgical high-speed steel (KHA30) with Vickers hardness of 840. All substrates were polished to mirror finish.

The specimen was a square plate with a side of 10 mm and 5 mm in thickness for the HCD coating, and a
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disc with a radius of 16 mm and thickness of 7 mm for the CA coating. Since the coated surfaces were slightly rough due to processing, the deposited specimens were given a light polish. The MSE tests were conducted within concentric circles of the specimen of about 8.5 mm in diameter to avoid any effect of test position.

2.3. Surface analyses

The specimen surfaces before and after the MSE tests were examined by scanning electron microscopy (SEM). In addition, the coated surfaces were analyzed with X-ray diffraction (XRD). An incident angle of 1° was used to minimize the penetration depth of the X-ray beam. A copper target was used, and the accelerating voltage was set to 40 kV, the beam current to 50 mA and the scanning speed to 4° min⁻¹.

Compositional depth profiles of coatings were obtained by a glow discharge optical emission spectroscopy (GDOES). It was done using the high frequency pulse mode and utilizing an anode of 4 mm in diameter.

Nano-scale hardness was measured by a nano-indentation using a Vickers pyramid. Electro-magnetic actuation was used and the displacement was measured by a capacitance gauge. The load was set at 98 mN.

3. Results and discussion

3.1. Morphology and properties of TiN/TiCN

Figure 3 shows SEM micrographs of fractured cross-sections of the TiN/TiCN coatings. In Fig. 3, the thicknesses of the interfaces between TiN and TiCN layers are roughly described by means of calotest measurements, see Table 1. A relatively coarse and pronounced columnar structure can be clearly observed for both coatings. However, the interfaces between TiN and TiCN layers were not clear.

Table 1  Details of the coating specimens

| Deposition system | Coating       | Substrate          | Thickness by calotest, µm | Hardness Nano-indentener (9.8 mN), HV | Roughness Ra, µm Initial surface |
|-------------------|---------------|--------------------|---------------------------|---------------------------------------|----------------------------------|
|                   | Coating      |                    | Coating | Individual |                               |                                  |
| HCD               | TiN/TiCN     | HSS (SKH51)        | 1.54     | (1.08/0.46) | 3316                           | 0.02                             |
|                   | TiN          |                    | 1.53     | -           | 2801                           | 0.03                             |
| CA                | TiN/TiCN     | P/M HSS (KHA30)    | 1.82     | (0.5/1.32)  | 3309                           | 0.08                             |
|                   | TiN          |                    | 2.15     | -           | 2782                           | 0.06                             |

Fig. 3  SEM micrographs of fractured cross-sections (The interface and the thickness of TiN/TiCN are described by the calotest measurement)

Fig. 4  XRD spectrum (TiN reference [12])
TiN/TiCN coatings. The characteristic peaks of TiN are also indicated in Fig. 4 as a reference [12]. Although the difference of each peak between TiN and TiCN is very small, it is found that only the peaks of the outer TiCN layer appeared on the XRD spectrum for both TiN/TiCN coatings. The influence of the inner TiN layer did not appear because of the small X-ray incidence angle. X-ray diffraction (XRD) analyses did not show any clear differences between HCD and CA coatings.

Figure 5 shows the results of the GDOES analysis. Although the time, indicated on the horizontal axis, and the depth from the top surface do not have a strict one-to-one correspondence, they are qualitatively proportional and thus indicates in the following. For the HCD coating, it is seen that the top and second layers were individual TiCN and TiN respectively with well-defined thicknesses. The profile of the TiCN layer indicates that the concentration of C changes gradually from TiCN to TiN layer. The concentrations of Ti and N were almost constant in the TiN layer. For the CA coating, the profiles were complicated. The concentration of Ti, C and N were almost constant from the top surface to a certain depth, but then the concentration of C shows a dip and the concentration of N has a peak. The TiN layer was found to be very thin between the TiCN layer and substrate. With a GDOES analysis, the depth resolution gets worse with increasing depth because the GDOES surface analysis involves sputtering of the surface material. Since two kinds of commercial coatings were used as the specimens in this study, their chemical structures and individual thicknesses of each layer were, unfortunately, different between the two coatings.

3.2. Erosion tests

Figure 6 shows the surface profiles of the erosion scar on the TiN/TiCN coatings, which were measured after various test durations. For both coatings, the erosion of the coating was gradual and slow until the coating was fully penetrated, upon which the erosion of the substrate commenced. When comparing the HCD coating and the CA coating, the eroded surface was smoother for the HCD coating than for the CA coating. At each test interval, the difference of depth between the original and the eroded surface was measured at the

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**Fig. 5** GDOES depth profiles

**Fig. 6** Surface profiles along the center-line of the erosion scar for TiN/TiCN coatings after various test time

(The interface and the thickness of TiN/TiCN are described by the calotest measurement)
The variations of erosion depth against test duration are plotted as shown in Fig. 7. In Fig. 7, the behaviors of single layer TiN coatings, deposited under the same conditions as the TiN layers of the two-layer coatings, are also shown. For the HCD coating, the erosion depth increased slowly at the beginning of the test and then almost linearly at a moderate slope until the TiCN layer was fully penetrated. After that the erosion rate increased remarkably. The obvious changes in the slope of the erosion curves clearly indicate the individual thicknesses of the TiCN layer and the TiN layer. For TiCN coating by CA, the erosion depth increased quickly at the beginning of the test, and then increased linearly until the TiN layer was reached; then, the erosion depth increased at a high slope. The increase of erosion depth at the beginning of the test may be caused by the rough original surface of the specimen. The results indicate that the MSE test is able to discriminate the erosion properties of the thin two-layer hard coatings, independent of the properties of the substrate.

The resolution of the evaluation of the MSE technique depends on the accuracy of the surface profile measurements, which was about 0.1-0.2 μm in this experiment. Thus the precise evaluation of the TiN layer of the CA coating was impossible because only a few measurement points were available in the layer. In addition, taking into account the deposition process, the change from TiN to TiCN in the fabrication process is done by replacing N₂ gas with CH₄ gas gradually, and thus there may be no clear interface between the TiN and TiCN layers. For these reasons, the TiN layer was not clearly resolved in this experiment for the CA coating.

The slopes of the each coating, except for the beginning of the test, were calculated by means of the least-squares method, and defined as the erosion rate in this study.

The values of the erosion rates of the individual TiCN and TiN layers, together with those of the single-layer TiN coating, are summarized in Table 2. It is found that the erosion rate of the TiN layer in the HCD specimen almost coincides with that of the single-layer TiN coating. For the CA specimen, a similar comparison was impossible because the TiN layer was too thin to calculate the erosion rate accurately.

The erosion rate of the TiCN layer was 38% of that of TiN layer for the HCD coating. The hardness, inferred with nano-indentation, was about 1.2 times...
higher for TiCN than for TiN, see Table 1. Generally the slurry erosion is known to be affected by not only hardness but also fracture toughness. However, the fracture toughness was not measured in this study and the qualitative relationship between erosion rate of the MSE test and fracture toughness was not clarified in our previous studies. The TiCN coatings are known to be have a fine columnar structure compared with TiN coatings [13]. From these points, the TiCN coating is considered to be better strength to erosive fracture than the TiN coating due to high hardness and fine columnar structure.

When comparing the TiCN layers of the HCD specimen and the CA specimen, the erosion rate of the HCD specimen was larger than that of the CA specimen, while both coatings showed almost the same value as the TiN single-layer coating. Because the chemical composition of the Ti, C and N elements was unknown by means of the analyses of the XRD and the GDOES in this experiment, it is impossible to simply compare the erosion rates of HCD and CA coatings. Taking these circumstances in consideration, the differences of the TiCN layer between the HCD and CA coatings are discussed in detail in the next section from the viewpoint of the eroded surface topography.

![Cross-section profiles of the TiN/TiCN coatings](image)

Fig. 8 Cross-section profiles of the TiN/TiCN coatings
(The interface and the thickness of TiN/TiCN are described by the calotest measurement)
3.3. Observation of eroded surfaces

The differences in topography of the eroded surfaces have become clear from the variations of the surface profiles measured with a surface profilometer, see Fig. 6. Here, the enlarged surface profiles corresponding to the points on the erosion curve of each layer are shown in Fig. 8. For the HCD coating, the erosion proceeded uniformly and produced a mostly smooth surface. For the CA coating, a pitted surface with many small hollow blemishes was observed. The hollow blemishes with a depth of more than 0.1 μm were counted over a length of 0.5 mm on the surface profiles. The results are summarized in Table 3. For the HCD coating, only a few hollow blemishes with a depth less than 0.3 μm were observed. On the other hand, for the CA coating, many deep hollow blemishes occurred and both the depth of individual blemishes increased with, as well as the total number of blemishes. The existence of the hollow blemishes may explain the difference in the erosion rates between the HCD and the CA coatings.

The differences in the profiles of the eroded surfaces between the HCD and CA coating could be quantified in the variation of the roughness parameters of peak height \( R_{pk} \) and peak valley \( R_{vk} \) [14] as is shown in Fig. 9. \( R_{vk} \) was much larger for the CA coating than for the HCD coating.

| Point of erosion curve | Number of hollows with depth X μm | Coated by HCD | Coated by CA |
|------------------------|----------------------------------|---------------|--------------|
|                        | 0.1 \( \leq X < 0.3 \) | 0.3 \( \leq X < 0.5 \) | 0.1 \( \leq X < 0.3 \) | 0.3 \( \leq X < 0.5 \) |
| 1                      | 0                                | 0             | 0            | 1            |
| 2                      | 0                                | 0             | 10           | 1            |
| 3                      | 1                                | 0             | 8            | 0            |
| 4                      | 5                                | 0             | 16           | 4            |

Fig. 9  Surface roughness of original and eroded surface in Fig. 8

(a) TiN/TiCN coated by HCD

(b) TiN/TiCN coated by CA

Table 3  The number of the hollow blemishes existed in the range of depth
The morphology of the eroded surfaces was investigated in detail with SEM observation. Figure 10 shows representative SEM photographs of the eroded surfaces of the TiCN layer, together with the original surfaces of both the HCD and CA coatings. For the HCD coating, small pits and blemishes are observed on the eroded surface as well as the original surface. For the CA coating, the original surface is smooth with small pits, but many large hollow blemishes appear on the eroded surface. Erosion proceeds in the direction of depth and also in the lateral direction by enlarging the pits and/or combining neighboring hollow blemishes. The hollow blemishes of the single layer TiN are different between the HCD and CA coating as well as TiN/TiCN coatings, see Fig. 11. The initial pits and/or the hollow blemishes may have been due to the macroparticles, i.e. droplets, which are due to the fabrication process. Generally, the CA process produces droplets emitted by the violent vaporization at arc spots on the cathode of Ti compared with HCD process [15,16]. Several effects, due to the existence of hollow blemishes, on the erosion rate are considered. However, because the chemical composition of the TiCN layer and the ratio of the thickness of TiCN to TiN layer differed between the HCD and CA coating in this study, it is difficult to compare their erosion rates on the basis of one factor, i.e. the existence of hollow blemishes. The effects of the existence of hollow blemishes on the MSE test results should be studied as a separate topic in a further study.

From these results, it is found that the measurements of the variations of the surface profiles in the MSE test can be used to evaluate the properties of the original fabrication process as well as the surface strength. Therefore the MSE test may be useful to evaluate the difference of the morphology of coatings caused by
fabrication method.

Further study is necessary to improve the apparatus with high resolution and/or automatic measurement system. In addition, more study on the morphology evaluation method based on the surface profiles is needed.

4. Conclusions

The Micro Slurry-jet Erosion (MSE) test was conducted to evaluate the surface strength properties of two-layer PVD TiN/TiCN coatings deposited by two techniques. The following conclusions are drawn.

(1) The MSE test did evaluate the individual erosion properties of TiCN and TiN layers independent of the substrate.

(2) The hardness of TiCN layers, coated by HCD or CA, was measured with nano-indentation and found to be approximately 20% higher than for TiN, the erosion rates of TiCN layers were found to be between 32% and 38% of the erosion rate of TiN.

(3) For the HCD coating, the erosion proceeded uniformly and produced a mostly smooth surface. On the other hand, for the CA coating, a pitted surface was observed. The existence of the hollow blemishes which caused by macroparticles i.e. droplets in the coating may affect the difference in the erosion rates between HCD and CA coatings.

(4) The MSE test may be useful to evaluate the difference of the morphology of coatings as well as the surface strength which are related with the fabrication process for multi-layer coatings.

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