IUMRS-ICA 2011

Structures and Properties of (TiAlSi)N Films

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Abstract
The current study uses cathode arc evaporation to coat TiAlSiN, TiN, and AlTiN multilayer films on tool surfaces. The specimens were examined by scanning electron microscopy to characterize film structures, thickness and compositions. Wear tests and nanoindentation tests were also performed to evaluate their coefficients of friction and thin film adhesion. Results show that TiAlSiN, TiN, and AlTiN multilayer films bear coefficients of friction 0.44, 0.32 and 0.39, respectively. The coefficient of friction for TiN film is lower mainly due to its lower surface roughness. Nanoindentation tests, on the other hand, show that the film hardness of TiAlSiN, TiN and AlTiN films are 37.4, 22.1 and 27.4 GPa, respectively. The hardness of TiAlSiN and AlTiN films are higher than that of TiN due to grain size strengthening. The three films all have HF1-HF4 level adhesion. On thermal stability of three coatings, TiAlSiN film is shown by X-Ray diffraction to withstand oxidation up to 900°C indicating that TiAlSiN has better high temperature stability. The different natures of three coatings can affect their performance and thus their applicability for cutting of different materials.

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Keywords: Cathode arc evaporation; nanoindentation; coefficient of friction; coatings; TiAlSiN/TiN/AlTiN multilayer

1. Introduction

Rapid development of technology requires continuous improvement on machining technology. To improve machining efficiency and to extend cutting tool life, the materials for cutting tools have been making constant progress. The advanced cutting tools can reduce both processing energy and material consumption, so there is continuous need to find better materials. Besides the cutting tool material itself, tool geometry and cutting parameters must also be taken into account.

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A lot of research has been made extensively on the hard coatings for cutting tools. These films include carbide, nitride, and oxides. By increasing the thickness of hard coatings on tool surface, tool life can be extended by several times. These wear-resistant layers for heavy-duty cutting blades are usually prepared using chemical vapour deposition (CVD) and physical vapour deposition (PVD). [1] [2]

In current study, cathodic arc evaporation (CAE) process is employed to prepare (Ti/Al/Si)N nitride films on tool steels. Their tribological properties are examined to understand the applicability of these hard coatings.

2. Experimental

2.1. Sample preparation

The current study uses 25.4mm diameter x 8mm thick M2 tool steels as substrate. For microstructure study, 304 stainless steels are chosen as substrate. The substrates are prepared by grinding, polishing, and cleaning prior hard coating deposition. Cathodic arc deposition process uses Ti and Al or AlSi target to co-deposition TiAlSiN, TiN, and AlTiN under N2/Ar atmospheres. The deposition process parameters are listed in Table 1 where the arc current of Ti target is controlled to fix at 60 A. The arc current for Al or AlSi target is controlled between 60 and 100 A to adjust the composition ratio of Al/Si and Ti.

Table 1 Specimen designations and process parameters.

| Sample   | Ti arc current (A) | Al/AlSi arc current (A) | Bias (V) |
|----------|-------------------|------------------------|----------|
| TiAlSiN  | -                 | (AlSi)60~100           | -120     |
| TiN      | 60                | -                      | -        |
| AlTiN    | -                 | (Al)60~100             | -        |

Glow discharge optical emission spectroscopy (GDOES) was employed to analyze the chemical composition of thin films using a LECO GDOES-750 optical spectrometer equipped with more than 40 channels and an optical monochromator. X-ray diffraction (XRD) was carried out using an X’Pert Pro MRD PANalytical spectrometer equipped with Cu-K source. The films were also heat treated at 700-900°C in air to test high temperature oxidation resistance of the three films. The coating structures and thickness are then characterized using JEOL JSM-7000F field emission scanning electron microscope (SEM). An energy dispersive spectroscopy is equipped for elemental analysis.

2.2. Nanoindentation test

Hardness (H) and reduced Young’s modulus \( (E' = E/(1-v^2)) \) of the coatings were determined by nanoindentation using a MTS NanoIndenter XP with Berkovich diamond tip. The tip was calibrated on a fused silica sample using the Oliver and Pharr method. The measurements of H and E’ as a function of the indentation depth were carried out using the continuous stiffness measurement (CSM) operation mode. At least five positions were tested for each set of sample to obtain average values. For film adhesion test, a Mitutoyo HR-521 Rockwell C tester using a loading of 150 kg is indented on the three films to compare their adhesion with substrate.
2.3. Ball-on-disc test

The tribological tests for the coatings were performed using a CSEM tribometer in ball-on-disc configuration. 5mm diameter WC ball was selected to grind on the coated samples which can avoid chemical reactions with the three coatings. On this tribometer, an actual dynamic friction coefficient was measured as function of testing time under servo-controlled normal load. The experimental parameters for the ball-on-disc wear tests use normal load of 2 N. The sliding velocities is fixed at 26.18 cm/sec, and the nominal diameter of wear track is 5 mm. Total sliding distance is 1000 m. All wear tests were performed under dry sliding conditions in air with 50–60 % relative humidity at room temperature.

3. Results and Discussion

3.1. Coating and compositional analyses

Thickness of TiAlSiN, TiN and AlTiN composite films are 2.0, 1.75, and 1.78 μm as analyzed by SEM observations. According to GDOES analyses, the TiAlSiN composite film coating contains about 35 to 45 at.% Ti, 15 to 25 at.% Al, ~4 at.% of Si, and 35 at.% of N. The TiN film consists of ~60 at.% of Ti and the rest N. AlTiN composite film then consists of 20 to 50 at.% Ti, 18~40 at.% of Al and ~35 at.% of N. The composition of Ti varied a greater range especially in the composite TiAlSiN and AlTiN films due to co-deposition of two targets. By adjusting arc current of Al or AlSi targets, the composition can be varied. Fig. 1 also shows that the distribution of Ti and Al fluctuates greatly. The higher Ti containing layers are designed to improve the adhesion of coatings with the substrate.

Fig. 2 shows the surface morphology of three films. The TiN film demonstrates least micro particles and cavities on surface and thus is smoother in contrast to TiAlSiN and AlTiN multi-layer films. Surface roughness measurement confirms this observation. The TiN film has a lowest surface roughness of 0.026 μm, while TiAlSiN bears the highest roughness as shown in Table 2. It is also important to note that the standard deviation for surface roughness of AlTiN is the greatest of three films indicating larger particles exist in this composite film.

Fig.1. Composition profiles of (a) TiAlSiN, (b) TiN, and (c) AlTiN films by GDOES measurements.
Fig. 2. Surface morphologies of (a) TiAlSiN, (b) TiN, and (c) AlTiN films.

Fig. 3 shows the cross sections of TiAlSiN, TiN, and AlTiN films. The coatings have dense columnar structures or their growth directions. Modulating contrast can be observed in Fig. 3(a) and (c) which correspond to Ti and Al compositional gradients designed to improve film adhesion in TiAlSiN and AlTiN multi-layer film structures, respectively. These modulating layers can also assist the increase of film hardness. From the adhesion test, it is seen in Fig. 4 that TiN film has the best adhesion in comparison with the other two composite films. Al or Al-Si apparently gives an adverse effect on film adhesion. The co-deposition of Al or Al-Si also gives rise to rough surfaces.

Fig. 3. Cross sections of (a) TiAlSiN, (b) TiN, and (c) AlTiN films.

Fig. 4. Film adhesion tests of (a) TiAlSiN, (b) TiN, and (c) AlTiN films using microhardness tester.
Table 2 Surface roughness of deposited films.

| Sample         | Surface roughness (Ra, µm) | Standard deviation, (µm) |
|----------------|----------------------------|--------------------------|
| TiAlSiN        | 0.125                      | 0.004                    |
| TiN            | 0.026                      | 0.002                    |
| AlTiN          | 0.076                      | 0.013                    |

3.2. XRD analyses

Fig. 5 shows the XRD analyses of TiAlSiN, TiN, and AlTiN films. The diffraction spectra are consistent with the literature [3-5] to bear NaCl structure. Both TiN and TiAlSiN shows a preferred (200) growing directions, while AlTiN composite film has weaker preferred orientations.

In order to understand the high-temperature oxidation characteristics, 700-900 °C heat treatments are performed. The XRD spectra of heat treated samples are also shown in Fig.5. Among the films, TiN sample shows surface oxidation at 700 °C temperature and the substrate starts to oxidize at 800 °C. In AlTiN sample, oxide structures appear in the XRD spectra at 800 °C and the substrate oxidize at 900 °C. TiAlSiN composite film can resist oxidation up to 900 °C in contrast to its bad adhesion. The surface is probably protected by the formation of thin dense Al and Al-Si oxide layers. From the heat treatment results, TiAlSiN composite film has the best oxidation resistance, AlTiN composite film the next, and TiN film has the least resistance to high temperature oxidation.

Fig. 5. XRD spectra of (a) TiAlSiN, (b) TiN, and (c) AlTiN films in as-deposited condition and after 700-900 °C heat treatments.

Fig. 6. Changes of coefficients of friction for three films with grinding distance.
3.3. Coefficients of friction measurements

Coefficients of friction can be measured through ball-on-disc tests. Fig. 6 shows that TiN film has the lowest coefficient of friction between 0.27 and 0.38. The TiAlSiN coating then demonstrates the highest friction coefficient between 0.42 and 0.45 among the three coatings. The coefficients of friction for different coatings appear to coincide with the surface roughness results in Table 2. The smoother TiN coating leads to lower friction while TiAlSiN has the rougher surfaces and thus larger friction.

3.4. Hardness measurement

Table 3 shows the hardness (H) and Young’s modulus (E) of TiAlSiN, TiN and AlTiN films by nano-indentation tests. The H / E values can be used as an indicator for the initiation of wear. Higher H/E value indicates greater resistance to abrasion with higher hardness prior a smaller amount of strain accumulation. From Table 3, AlTiN film bears the highest H/E value, and TiAlSiN film demonstrates the lowest H/E values among the three films investigated. However, TiAlSiN has the higher hardness than the other two films indicating its applicability for machining harder materials.

Table 3 Results of nanoindentation tests.

| Sample   | Hardness, H (GPa) | Young’s modulus, E (GPa) | H/E   |
|----------|-------------------|-------------------------|-------|
| TiAlSiN  | 37.39             | 547.48                  | 0.068 |
| TiN      | 22.14             | 295.42                  | 0.074 |
| AlTiN    | 27.44             | 323.86                  | 0.084 |

4. Conclusions

TiAlSiN composite hard coating can withstand high-temperature oxidation up to 900 °C and bears the highest hardness among the three films studied. It, however, has the highest roughness giving rise to a higher coefficient of friction. Less favourable adhesion is also observed. Its higher hardness could be applicable for harder material machining. TiN coating demonstrates smooth surface and low coefficient of friction. On the other hand, it has lower resistance to high temperature oxidation and oxidizes at temperature as low as 700°C possibly due to the lack of Al2O3 protection. The good adhesion of TiN might be useful for machining of tough materials such as stainless steels. The AlTiN has modest high temperature stability and intermediate roughness while keeping a high H/E value. Therefore, AlTiN can be employed for general material machining.

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