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Deposition and high temperature oxidation characteri ation of CrAlSiN thin films

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Abstract

Thin films of CrAlSiN were deposited on SKD11 tool steel substrate using Cr and AlSi cathodes by a cathodic arc plasma deposition system. The influence of process parameters on the deposited film properties were investigated. The oxidation characteristics of the films were studied at temperatures ranging from 800 and 1000⁜C up to 50 h in air. The films showed superhardness and good oxidation resistance..

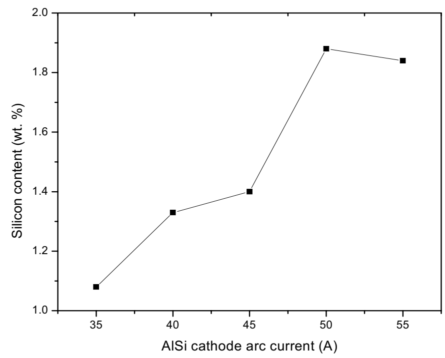
1. Introduction

TiN films have been widely used as hard wear resistant coatings for cutting tools. TiAlN films have been commercially successful particularly for high speed machining applications due to its improved oxidation resistance and hardness. However, the wear performance of TiAlN coating under ambient condition shows insignificant improvement due to its high friction coefficient. Similar to TiN, CrN has been successfully used and CrAlN resulted in even higher oxidation resistance than TiAlN. Further research to improve the oxidation resistance and mechanical properties of these coatings led to development of CrSiN, CrAlSiN. These films have been deposited by magnetron sputtering or hybrid method combining cathodic arc and magnetron sputtering. Because of the semi conducting properties of silicon, it was not possible to deposit silicon directly using a cathodic arc method, however we deposited TiAlSiN films by a cathodic arc process using Ti and AlSi cathodes. By expanding this approach, we were successful in depositing CrAlSiN films by a conventional cathodic arc plasma deposition process using two cathodes of chromium and aluminum silicon. We also studied high temperature oxidation of this film.

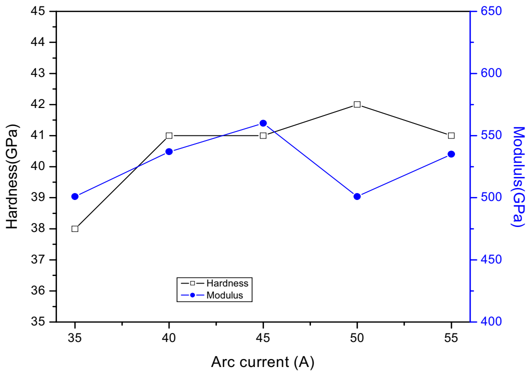
2. Experimental Procedures

CrAlSiN films were deposited on SKD11 tool steel (1.5%C, 11.5%Cr. 0.8%Mo, 0.9%V) substrate by typical cathodic arc plasma deposition equipment. AlSi alloy (12 at. % Si) and Cr were used for cathodes. The arc current of Al Si cathode and bias voltage were varied to determine the influence of these parameters on the structure and mechanical properties of the films. The phases and chemical composition of the films were determined by an X ray diffractometer and an electron probe microanalyzer. Morphology was observed by an optical microscope and a field emission scanning microscope. The films structure and the period of multilayers were investigated by a transmission electron microscope with an energy dispersive X ray microanalysis system. A computer controlled nanoindentor was used to measure the hardness of the films.. The oxidation experiments on the coated specimens were carried out using a thermogravimetric analyzer (TGA) between 800 and 1000 oC up to 50 h in 1 atm of air. The specimens were inspected by EPMA, AES, XPS, and XRD

3. Results and discussion



(a)



(b)

Fig. 1 Effect of AlSi current on the Si content (a) and hardness of CrAlSiN films (b) (pressure 4 Pa, bias voltage -100 V, temperature 300 °C, Ti cathode arc current 55 A, substrate rotation speed 4.55 rpm).

To determine the effect of silicon content in the film, the aluminum-silicon cathode arc current was varied from 35 A to 55 A. The films were deposited at a pressure of 4 Pa and a temperature of 300°C. The silicon content of the film increased with the aluminum-silicon cathode arc current, resulting in an increase of the hardness of the films (Fig. 1a). The hardness of the films increased with aluminum-silicon cathode arc current from 35 A to 50 A. A further increase in the aluminum-silicon cathode arc current decreased the hardness. The highest hardness of 42 GPa was obtained at a current of 50 A (Fig. 1b).

The effect of bias voltage on the hardness of CrAlSiN films was studied. The hardness of the film increased with the increase of the bias voltage up to -100 V. Further increase of the bias voltage decreased the hardness of the films. Cross-sectional TEM images of the CrAlSiN films deposited with various bias voltages (Fig. 2) indicated a nano-multilayered structure of the film. The films with sharp interfaces showed high hardness whereas the films with diffuse interfaces showed low hardness. For the sample deposited without bias voltage, the period was broad and the interfaces were rough, and the hardness was low (Fig. 2a). Fig. 2c shows that the interfaces are very rough. The rough interfaces decreased hardness even though the period is small. Energy dispersive X-ray microanalysis of CrAlSiN in the TEM demonstrate the presence of chromium in the bright layers, aluminum and silicon in the dark layers (Fig. 3) revealing a multilayered structure in which the nano-crystalline CrN layers alternate with nano-amorphous AlSiN layers. The hardness of the films was enhanced by forming this nano-scaled multilayer structure.

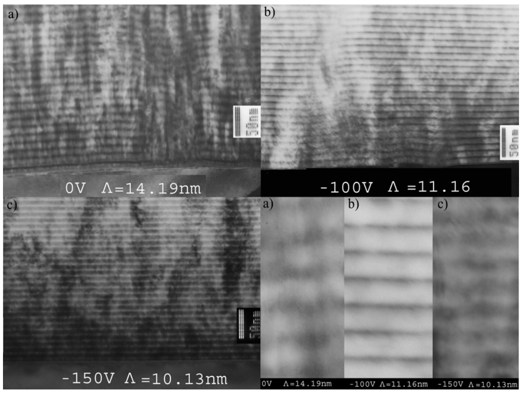


Fig. 2 Cross-sectional TEM image of the CrAlSiN multilayer with various bias voltages (a: 0 V, b: -100 V, c: -150 V).

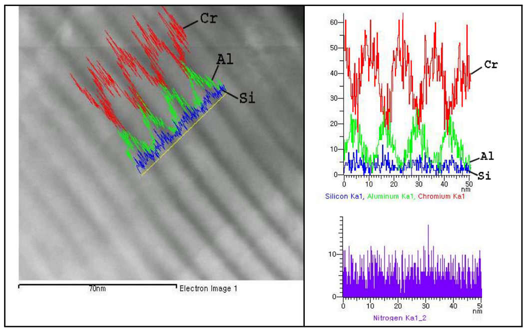


Fig.3 The EDX spectrum of the CrAlSiN multilayered film.

In the XRD results of the CrAlSiN film after oxidation, the substrate peaks were strong because the oxidation at 800 °C for 100 h was a mild oxidizing condition for CrAlSiN. Only CrN was detected in the unoxidized film. The diffraction patterns were diffuse and broad, because of small extent of oxidation and the formation of nanocrystalline oxide grains. As the oxidation progressed further, the substrate peaks became weaker and oxide grains grew. The oxidation at 1000 °C for 50 h resulted in the almost complete oxidation of the film. The intensity of α-Al_2O_3 was weaker than that of Cr_2O_3, due partly to the initially smaller amount of Al, and the partial dissolution of Al_2O_3 in Cr_2O_3. SiO_2 was not detected in any case, owing to its amorphous nature.

With the AES depth profiles of the CrAlSiN film, it can be seen from the location of Pt that oxygen diffused inwardly to react with Cr, Al, and Si. However, Cr and Al tended to diffuse outwardly toward the film surface.

With the study of the oxidation kinetics of the CrAlSiN-coated specimens, total weight gains were small and it was found that the CrAlSiN film has good oxidation resistance.

4. Conclusion

CrAlSiN films were deposited on SKD11 **tool steel substrate** by cathodic arc plasma deposition method. The films had a multilayer structure with alternating nano-crystalline CrN layers with armorphous AlSiN layers. The hardness of the films changed with the nitrogen gas pressure. Maximum hardness was observed at the pressure of 4 Pa. The hardness of the films also changed with the aluminum-silicon arc current; the films deposited at 50 A exhibited the maximum hardness. These films showed the most notable XRD peak broadening. The period of the films decreased with the increase of bias voltage. The hardness of the films changed with bias voltages. The maximum hardness was observed on the films deposited at bias voltage of -100 V and was accompanied by smooth interfaces. The maximum hardness was 42 GPa at the substrate rotation speed of 11.43 rpm.

During oxidation of CrAlSiN, Cr and Al diffused outward to a certain extent to form the surface scale. Si was relatively immobile. At the same time, oxygen diffused inward, whereas nitrogen diffused outward. The film displayed good oxidation resistance up to 1000 ^{o}C, to due the formation of Cr_2O_3, α-Al_2O_3, and amorphous SiO_2. These oxides existed as an oxide mixture.

Acknowledgment

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References

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