XPS analysis of SiC films prepared by radio frequency plasma sputtering

Y.-Y. Wang\textsuperscript{a}, K. Kusumoto\textsuperscript{b}, C.-J. Li\textsuperscript{a}

\textsuperscript{a} State Key Laboratory for Mechanical Behavior of Materials (Xi’an Jiaotong University), Welding Research Institute, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an710049, China
\textsuperscript{b} Dept. of Mechanical Systems Engineering, Engineering Faculty of Gunma University, Gunma 376-0052, Japan

Abstract

SiC films were deposited by radio frequency (r.f.) plasma sputtering (SPF-312H) on Ti6Al4V substrate with a pre-deposited Cr bond layer. The effects of sputtering parameters on the microstructure and the chemical bonds of the SiC films were investigated using X-ray photoelectron spectroscope (XPS, Perkin Elmer ESCA5600), atomic force microscopy (AFM, HITACHI WAO200), scanning electronic microscopy (SEM, JEOL JSM-5310) and X-ray diffraction (XRD RIGAKU RINT 2000/PC). The Vickers microhardness of the films was examined by a microhardness tester (MVK-H2) equipped a microscope with a magnification of 1000 at 25 gf loads. It was found that the sputtered Si-C films are amorphous on Ti6Al4V under the present deposition conditions. According to XPS analysis, the films almost consist of higher energy C-Si bonds under the higher power and lower chamber pressure. The bond structure hypothesis is well consistent with our previously achieved experimental observations concerning the evolution of surface roughness and microhardness with varying the sputtering power and chamber pressure.

© 2012 Published by Elsevier B.V. Selection and/or peer review under responsibility of Chinese Vacuum Society (CVS).
Open access under CC BY-NC-ND license.
Keywords: SiC; Film; Chemical bond; XPS; Radio frequency plasma sputtering;

1. Introduction
Titanium alloy Ti-6Al-4V finds wide application in aircraft, aerospace and biomedicine due to its high specific strength and biocompatibility [1]. However, the wear performance (low wear resistance and high friction coefficient) is unsatisfactory [2]. It is very promising that sputtered SiC films as protective coatings against the wear of Ti6Al4V alloy to improve their mechanical properties due to their outstanding high hardness and wear resistance [3]. The mechanical performances for sputtered SiC films depend strongly on their microstructure and phase structure. However, few researches have been reported on the microstructure and the chemical bonds in SiC films prepared on Ti-6Al-4V substrate by RF plasma sputtering technique. Therefore, in this study, the objective is to investigate the effects of sputtering parameters on the microstructure and the chemical bonds of the SiC films using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), in order to establish the relationships between the sputtering parameters, structure and microhardness and wear performances of SiC films on Ti6Al4V substrates.

2. Experimental materials and procedures

2.1 Sputtering deposition procedures

All the experiments were carried out with a commercial r.f. sputtering equipment (SPF-312H). A SiC plate in diameter of 4 inches was used as a target. Pure Ar was applied as operating gas. The sputtering parameters during deposition are listed in Table 1.

Table 1 Parameter variations during deposition

| Target: SiC, Cr |
|----------------|
| Substrate: Ti6Al4V (3 mm thick) |
| Power (W): 100, 200, 300, 400 |
| Sputtering time (min): 30, 60, 90, 120,160, 190 |
| Chamber pressure (Pa): 0.28, 0.5, 1, 3, 5, 7 |
| Deposition distance (mm): 40 |

SiC films were deposited on Ti6Al4V polished substrates with roughness of 0.047 μm, which were cleaned in an acetone solvent with ultrasonic auxiliary prior to inserting them into the deposition chamber. Once the specimens were put into the chamber, they were exposed to Ar+ ion etching for 10 min to further clean the surface of the samples in order to improve adhesion between the deposited film and substrate.

2.2 Film characterization

The microstructure was observed by scanning electronic microscopy (SEM). The surface morphology of the deposited films was examined by atomic force microscopy (AFM). The Vickers microhardness of the films was examined by a microhardness tester (MVK-H2) equipped a microscope with a magnification of 1000. An average of ten readings performed at 25 gf loads holding for 20 s on film surface was recorded for each specimen. The phase structure in the films was analyzed using X-ray diffraction (XRD) using an X-ray diffractometer (RIGAKU RINT 2000) with Cu Kα radiation. The composition and chemical bonding states of Si-C films were determined using XPS (Perkin Elmer ESCA5600). A monochromated
Mg Kα (1253.6 eV) X-ray radiation was used. The pass energy of the spectrometer was 23.50 eV. Before all measurements, the line position C 1s (284.5 eV) of HOPG was used as a binding energy reference. The films were subjected to Ar ion etching for 5 min to remove away the surface contaminants. The broad C 1s and Si 2p peaks are deconvolved with Gauss distribution function and the fitted curves have degree of confidence higher than 0.98.

3. Results and discussion

3.1 Effect of pressure on the microstructure of SiC film

Fig. 1 The cross-sectional microstructure deposited under the chamber pressure of 0.5 Pa (a) and 5 Pa (b)

Fig. 1 shows the typical microstructure of SiC film under the different chamber pressure. The middle brighter thin layer is a bond layer of Cr film, which was deposited directly onto the Ti6Al4V substrate prior to depositing SiC film. The bond layer was designed purposively to improve the adherence of sputtered SiC film and the Ti6Al4V substrate. The lower domain was the Ti6Al4V substrate and the upper area the SiC film. It is found that all the SiC films with very dense microstructure were successfully prepared by r.f. plasma sputtering on the pre-deposited Cr bond layer. Moreover, the film thickness was slightly increased with increasing the pressure. Because the higher pressure means the higher Ar ion concentration, therefore the more Si and C atoms are sputtered out off the target by Ar ion. However, during their traveling on the substrate, the possibility of the sputtered Si and C atoms colliding with each other, Ar and Ar ion also becomes more significant. It leads to the effective deposition of Si and C atoms.
decreasing. Consequently the deposition rate of SiC film prepared under the higher pressure is just a little higher than that under the lower pressure.

3.2 Effect of pressure on the surface morphology of SiC film

Fig. 2 shows the typical AFM images of the sputtered SiC films. It is obvious that the surface roughness of SiC films increases with increasing the pressure (The evident regular burrows in figures are scratches left on the substrate after polishing). The kinetic energy of sputtered particles can be estimated by the following relationships:

\[ U_k = \frac{D_w V_s}{P^{0.5}} \]  

Where \( U_k \) is the kinetic energy, \( D_w \) the target power density, \( V_s \) the substrate bias and \( P \) is the pressure. It is evident that the kinetic energy of sputtered Si and C atoms decreases with increasing the pressure. Comparing the AFM observations, it means the lower surface roughness or smooth surface is corresponding to the SiC films formed with the sputtered Si and C atoms of the higher kinetic energy. Therefore, the smoother surface indicates the higher density of SiC films while the rougher surface indicates the lower density [4].

![Fig. 2 Effect of pressure on the surface morphology of SiC films ((a) 0.28 Pa, (b) 0.5 Pa, (c) 1 Pa, (d) 3 Pa, (e) 5 Pa, (f)7 Pa)](image)

3.3 Effect of pressure on the microhardness of SiC film

Our previous study indicates the microhardness was hardly varied when the thickness exceeded about 5 µm. Under the same pressure and film thickness, the higher power led to higher microhardness than the lower power. Moreover, with decreasing the pressure, the microhardness was increased (as shown in Fig.3). The reason may be that the relatively high pressure resulted in Si-C films with a less dense structure due to the lower surface mobility of Si and C atoms. When the power was 400 W and chamber pressure was 0.28 Pa, the SiC films had the average highest HV 2813 ranged from HV 2606 to HV 3087, which was over 10 times higher than that of Ti6Al4V and comparative to sintered SiC bulk materials.

3.4 Phase structure of SiC film
Fig. 4 shows a typical XRD diffraction pattern of SiC film with 9.13 \( \mu \)m thick sputtered with the power of 400 W and the chamber pressure of 5 Pa for 160 min. The first diffuse scattering peak appears around 2035.5°, which corresponds to the strongest peak of \( \beta \)-SiC. It is indicated that Si-C in the film presents in amorphous phase. The second broaden peak (around 20 44.4°) is corresponding to the strongest peak of body-centered cubic Cr. The Cr bond layer was used to improve the adhesion between the films and Ti6Al4V substrate. Similarly, Cr exists in amorphous state.

Fig. 3 Effect of the pressure on the microhardness of the SiC film with the thickness of 5.1 ~ 5.4 \( \mu \)m

Fig. 4 XRD patterns of SiC film and Ti6Al4V

3.5 XPS analysis of SiC film

Because there are contaminates and oxides on the SiC film surface, ion sputter-etching was used to remove them during XPS applied to identify and determine the concentration of the elements in the films. Fig. 5 shows the survey spectra of the film before and after ion sputter-etching for 8 min. it is found that after etching the O concentration is significantly decreased and the film is primarily composed of C and Si (a few Ar elements are trapped in the film).
Fig. 5 XPS survey spectra of SiC film

Fig. 6 C 1s (a) and Si 2p (b) core levels in XPS spectra of SiC films before ion etching (400 W, 0.28 Pa)

For crystalline SiC, the typical binding energy of C 1s and Si 2p is 280.7-283.0 eV and 99.7-100.8 eV, respectively. Before etching, the high-resolution spectra of the film shows evidently the spin-orbit splitting of the C 1s and Si 2p (Fig. 6) because there exist plenty of O atoms and the structure defects producing during sputtering. Three binding energy peaks of Si 2p are 98.6 eV, 99.95 eV and 101.98 eV,
corresponding to the one of Si 2p in Si-Si, Si-C and C-O-Si chemical bond, respectively. Correspondingly, three binding energy peaks of C 1s are 282.5 eV, 284.5 eV, 286.1 eV, corresponding to the one of C 1s in C-Si, C-C and C-O bond, respectively. However, after etching for 2 min, the film almost comprises C and Si elements (Table 2). In addition, the atomic ratio of Si/C in the sputtered film on the Ti6Al4V substrate is approximately 1:1 to be stoichiometric.

| Table 2 Atomic concentration (%) in the SiC film |
|-----------------------------------------------|
|                                | 1s | Si 2p | O 1s |
| No ion etching                  | 54.25 | 26.93 | 25.12 |
| Ion etching for 2 min            | 48.05 | 47.38 | 4.57  |
| Ion etching for 5 min            | 48.23 | 47.72 | 4.05  |

![Fig.7 High resolution spectra of SiC film after ion etching ((a),(b) 400 W, 5 Pa; (c),(d) 200 W, 5 Pa)]

After ion etching, spin-obit splitting almost disappears. The bonding energy of C 1s and Si 2p stands primarily in the typical ranges under higher power (Fig 7. (a) and (b)). It is indicated that C and Si atoms form stronger C-Si chemical bond in the film. However, under lower power, C 1s and Si 2p peaks present evidently chemical shifts (Fig 7. (c) and (d)). It is implied that the sputtered Si-C film formed by the relatively weak chemical bonds [5,6].

4. Conclusions
SiC films with dense microstructure are successfully prepared by r.f. plasma sputtering on Ti6Al4V with a pre-deposited Cr bond layer. R.f. plasma sputtered Si-C films are amorphous under the present deposition conditions.

According to XPS analysis of prepared films, the sputtered film is almost composed of Si and C elements. The further analysis to the atomic concentration indicates that the ratio of Si and C atoms in the film is approximately 1:1 and the same as the target composition.

Before ion etching, the Si-C bond, C-C bond and C-O-Si bond are dominant, and a small number of Si-Si bonds still exist in the surface of the sputtered films. However, after etching the films almost consist of higher energy C-Si bonds under the higher power and lower chamber pressure. The bond structure hypothesis is well consistent with our previously achieved experimental observations concerning the evolution of surface roughness and microhardness with varying the sputtering power and chamber pressure.

5. Acknowledgement

This project was supported by Advanced Technology Research Center (ATEC) of Gunma University in Japan. Special thanks are due to A. Professor K. Itoh, S. Furusawa and S. Kuroda for supporting our experiments and beneficial discussion and suggestions.

6. Reference

[1] J.C. E. Bocardo, M.A.L. Heredia, D.A.C. Hernandez, et al, Azojomo 1 (2005): 1-15
[2] J.Qu, P.J. Blan, T.R. Watkins, et al, Wear 258 (2005): 1348-1356
[3] J.C. Oh, E.Yun, M.G. Golkovski, S. Lee, Materials Science and Engineering A 351 (2003): 98-108
[4] Soon-Eng Ong, Sam Zhang, Hejun Du, Deen Sun, Diamond and Related Materials 16 (2007) : 1628 – 1635
[5] Y. Awad, M.A. El Khakani, C. Aktik, et al, Surface & Coatings Technology 204 (2009): 539 – 545

7. Kun Xue, Li-Sha Niu, Hui-Ji Shi, Jiwen Liu, Thin Solid Films 516 (2008): 3855 – 3861

Acknowledgement

This project was supported by Advanced Technology Research Center (ATEC) of Gunma University in Japan. Special thanks are due to A. Professor K. Itoh, S. Furusawa and S. Kuroda for supporting our experiments and beneficial discussion and suggestions.

8. Reference

[1] J.C. E. Bocardo, M.A.L. Heredia, D.A.C. Hernandez, et al, Azojomo 1 (2005): 1-15
[2] J.Qu, P.J. Blan, T.R. Watkins, et al, Wear 258 (2005): 1348-1356
[3] J.C. Oh, E.Yun, M.G. Golkovski, S. Lee, Materials Science and Engineering A 351 (2003): 98-108
[4] Soon-Eng Ong, Sam Zhang, Hejun Du, Deen Sun, Diamond and Related Materials 16 (2007) : 1628 – 1635
[5] Y. Awad, M.A. El Khakani, C. Aktik, et al, Surface & Coatings Technology 204 (2009): 539 – 545
[6] Kun Xue, Li-Sha Niu, Hui-Ji Shi, Jiwen Liu, Thin Solid Films 516 (2008): 3855 – 3861