I O U R N A L O F

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Synthesis and mechanical properties of Ti-Si-B-N coatings by a PECVD technique

Woo Jin Lim^a, Dong-woo Shin^d, Jung Ho Shin^b, Se Hun Kwon^b, Qimin Wang^{b,c,*} and Kwang Ho Kim^{a,b,*}

^aSchool of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea

^bNational Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 609-735, Korea

^cSchool of Mechanical and Electronic Engineering, Guangzhou University of Technology, Guangzhou 510006, P.R. China

^dSchool of Nano & Advanced Materials Engineering, Gyeongsang Natioanl University, Jinudaero 501, Jinju, Gyeongnam 660-701. Korea

Ti-Si-B-N coatings were deposited on AISI 304 substrates by plasma enhanced chemical vapor deposition using a gas mixture of TiCl₄, BCl₃, SiH₄, N₂, H₂, and Ar. Coatings with different Si and B contents were obtained by varying the gas ratio of BCl₃/SiH₄. The Si-free Ti_{0.75}B_{0.25}N coating exhibited nanocomposite microstructure of Ti (B, N) crystallites and amorphous BN phase. With increase of Si in the coatings, the nanocomposite microstructure consisting of nano-sized (Ti, Si)(B, N) crystallites and amorphous BN/Si₃N₄ tissue phase was obtained in the coatings. The microhardness of the Ti-Si-B-N coatings increased from ~38 GPa for the Ti_{0.75}B_{0.25}N, and then decreased with further increase of Si content in the film. All the Ti-Si-B-N coatings exhibited friction coefficient less than 0.5. The Ti_{0.74}Si_{0.04}B_{0.21}N coatings showed the lowest average friction coefficient of 0.4. The relationship between chemical composition, microstructure and properties of the Ti-Si-B-N coatings were discussed.

Key words: Ti-Si-B-N, Nanocomposite, PECVD, Multi functional, Friction coefficient.

Introduction

Recently, nanocomposite Ti-Si-N and Ti-B-N coatings by both physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PECVD) have been widely studied due to their superior mechanical properties, such as high hardness and good wear properties compared to conventional TiN coatings [1-3]. These superior mechanical properties originate from their unique nanocomposite microstructures, which consist of nano-sized TiN crystallites embedded in a Si_3N_4 or BN (or TiB₂) amorphous matrix by thermodynamically driven spinodal decomposition (phase segregation) [4-5]. The microstructure and mechanical properties are affected mainly by the B and Si content due to a change in the volume fraction of amorphous BN and Si₃N₄ phases and a crystal size reduction effect. The effects of amorphous Si₃N₄ and BN phases of both Ti-Si-N and Ti-B-N coatings on the microstructure evolution and mechanical properties have been investigated by many researchers [6-7].

The quaternary Ti-Si-B-N system can be tailored to have superior properties by combining the merits of both Ti-Si-N and Ti-B-N coatings. A few papers reported on the Ti-Si-B-N coatings prepared by PVD methods. D.V Shtansky et al. reported that the Ti-Si-B-N coatings deposited by PVD exhibited high microhardness (\geq 25 GPa) and good toughness [8-9]. However, there are no reports on Ti-Si-B-N coatings deposited using a PECVD technique until now. In this study, Ti-Si-B-N coatings were deposited on AISI 304 substrates by PECVD using a TiCl₄, BCl₃, SiH₄, H₂, N₂ and Ar gas mixture. Microstructure and mechanical properties of the coatings were investigated systemically by changing the B and Si contents in the coatings.

Experimental

Coating deposition

Quaternary Ti-Si-B-N coatings were deposited on AISI 304 substrates by PECVD technique using a gaseous mixture of TiCl₄, BCl₃, SiH₄, H₂, N₂ and Ar. The schematic diagram of the PECVD apparatus and its details were depicted in our previous work [10]. Based on our precedent work, the Ti_{0.75}B_{0.25}N coating was selected as the base coating. The SiH₄ gas with varying ratio between BCl₃ and SiH₄ was added in the gas mixture to deposit Ti-Si-B-N coatings with various Si and B contents. The typical deposition conditions for

Table 1. Typical deposition conditions for the Ti-Si-B-N coatings.

Total flow rate	70 sccm
Working gas ratio [N ₂ /H ₂ /Ar]	6/34/30 sccm
Deposition pressure	133.3 Pa
Deposition time	1 hr
R.F. power	180 W
Deposition temperature	600
Input gas ratio, $Rx = [SiH_4/(BCl_3+SiH_4)]$	0~100%

^{*}Corresponding author:

Tel:+82-51-510-2391

Fax: +82-51-510-3660

E-mail: qmwang@pusan.ac.kr ; kwhokim@pusan.ac.kr

Ti-Si-B-N coatings are showing in table 1.

Characterizations

The film thickness was determined by cross-sectional observations using a field emission scanning electron microscope (S 4800, Hitachi). The compositional analyses of the Ti-Si-B-N coatings were carried out using an electron probe microanalyzer (EPMA 1600, Shimadzu). An X-ray diffractometer (XRD, D8, Bruker) using a CuKa radiation was utilized to investigate the crystal structure of Ti-Si-B-N coatings. The chemical bonding status of the coatings was obtained from an X-ray photo electron spectroscopy (XPS, VG Scientifics, Escalab 250). The selected coating was observed by a high-resolution transmission electron microscopy (HRTEM) using a field emission transmission electron microscope (FE-TEM, Jeol, JEM-400FX) with a 400 KV acceleration voltage. The hardness was evaluated a microhardness tester with a



Fig. 1. EPMA result as a function of SiH₄ Rx.

Knoop indenter (Matsuzawa, MMT-7) under a load of 25 g. The friction coefficient was evaluated through sliding wear test using a conventional ball-on-disk wear apparatus. A steel ball (diameter 6.34 mm, 700 H_v 0.2) was used as a counterpart material. The sliding tests were conducted with a sliding speed of 0.157 m/s under a load of 5 N at ambient temperature (around 24 °C) and a relative humidity of 25~30%.

Results and discussion

Microstructure of the Ti-Si-B-N coatings

Ti-Si-B-N coatings were deposited with various Si content by systemically varying the input gas ratio, $R_x = [SiH_4/(SiH_4 + BCl_3)] \times 100$, at a deposition temperature of 600 °C and a RF power of 180 W. Fig. 1 shows the changes in the Ti, Si, B, N, and Cl content in the Ti-Si-B-N coatings. The Si content in the Ti-Si-B-N coatings increased gradually from 0 (Ti_{0.75}B_{0.25}N deposition condition) to 10.3 at.% with increasing R_x value but the B content in the Ti-Si-B-N coatings decreased from 11.41 to 0 at.%. On the other hand, Ti and N contents in the Ti-Si-B-N coatings were relatively constant, and the residual Cl content in the coatings was maintained at ~ 1 at.%. Fig. 2(a) shows the XRD patterns of the Ti-Si-B-N coatings. Only the XRD peaks identified as TiN (200) were detected as the peaks from the coatings. The other peaks belonged to the substrates. No XRD peaks corresponding to Si₃N₄, TiSi₂ and TiB₂ phases were found peaks. It can be seen that the TiN (200) peaks in the Ti-Si-B-N coatings shifted to a high angle and the FHWM values decreased with increasing the Si content, Si/(Si+B). Therefore, Si and B should exist in an amorphous phase or are dissolved in a TiN crystal. Fig. 2(b) shows the interplanar distance, d_{200} , of the TiN (200) crystal plane and the grain size of the Ti-Si-B-N coatings as a function of the Si content, Si/(Si+B), in the coatings. The interplanar distance and grain size was calculated by Bragg's law and the Scherrer equation, respectively



Fig. 2. (a) XRD patterns and (b) d₂₀₀ values of (200) crystal plane and grain size of Ti-Si-B-N coatings as a function of Si content.



Fig. 3. XPS spectra near the binding energy of N1s for (a) $Ti_{0.75}B_{0.25}N$ and (b) $Ti_{0.74}Si_{0.04}B_{0.21}N$ coatings.



Fig. 4. XPS spectra near the binding energy of (A) B1s and (B) Si2p for (a) Ti_{0.75}B_{0.25}N and (b) Ti_{0.74}Si_{0.04}B_{0.21}N coatings.

[11-12]. The d_{200} values decreased from 2.1291 Å for the $Ti_{0.75}B_{0.25}N$ coatings to 2.1105 Å for $Ti_{0.76}Si_{0.24}N$ with increasing Si content, Si/(Si+B) in the coatings. The d_{200} values showed a minimum value at approximately Si 7.8 at.% which remained relatively constant with further increases in the Si content. As shown in Fig. 2 (b), the $Ti_{0.75}B_{0.25}N$ coatings had a larger d_{200} value, 2.1291 Å, than that of pure TiN, 2.1190 Å (JCPDF 87-0633). This larger d_{200} value of Ti_{0.75}B_{0.25}N coatings suggests that B atoms are dissolved in the TiN crystal lattice to form a Ti (B, N) crystal. The decreased d_{200} with increasing Si content, Si/(Si+B), suggests that the Si atoms were dissolved in the Ti (B, N) crystal lattice, where smaller Si atoms substituted the Ti atoms. The solubility limit of Si in the Ti-B-N coatings seems to be approximately 7 at.% considering that the d_{200} value did not decrease with further increases in the Si content. On the other hand, in Fig. 2(b), the grain size of the Ti-Si-B-N coatings increased gradually from approximately 13.7 nm to 36 nm with increasing Si content, Si/(Si+B), from 0 to 10.3 at.%. The increased grain size indicates that the grain size of Ti-Si-B-N coatings is affected mainly by the Si content in the coatings.

The chemical binding status in the Ti-Si-B-N coatings was examined by X-ray photoelectron spectroscopy (XPS). The binding energies were calibrated with the C 1s peak (284.5 eV) for free carbon. Fig. 3 shows the XPS spectra near the binding energies of N 1s for the (a) $Ti_{0.75}B_{0.25}N$ and (b) $Ti_{0.74}Si_{0.04}B_{0.21}N$ coatings. In the case of Ti_{0.75}B_{0.25}N coating (Fig. 3(a)), two peaks at binding energies of 396.1 eV and 397.9 eV were observed, which are in good agreement with those of the TiN and BN phase [13-14]. As shown in Fig. 3(b), a peak corresponding to 397.5 eV was also observed, which is in good agreement with that of the Si₃N₄ phase [13]. As shown in Fig. 4(a), a peak corresponding to the BN phase at 190.3 eV [14] was observed. The peak for the Ti_{0.75}B_{0.25}N coating was higher than that for the Ti_{0.74}Si_{0.04}B_{0.21}N coatings, which indicates that there was a larger amount of the BN phase in $Ti_{0.75}B_{0.25}N$ than in $Ti_{0.74}Si_{0.04}B_{0.21}N$. Considering that the peak corresponding to Si₃N₄ (101.8 eV [13]) was observed only in the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coatings, as shown in Fig. 4(b), it can be concluded that the decrease in the BN peak of the Ti_{0.74}Si_{0.04}B_{0.21}N coating is strongly related to the formation of a Si₃N₄ phase. XPS showed that B and Si existed mainly as BN



Fig. 5. (a) DF-TEM (with SADP) and (b) HR-TEM of $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating.

and Si_3N_4 phases in the Ti-Si-B-N coatings, which was considered to be amorphous according to the XRD pattern in Fig.2(a). XRD and XPS analyses suggest that the ternary $Ti_{0.75}B_{0.25}N$ coatings consists Ti (B,N) nanocrystals and amorphous BN phase, while the quaternary Ti-Si-B-N coatings are composites consisting solid-solution (Ti,Si)(B,N) crystallites and amorphous BN/Si₃N₄.

The microstructure of the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating was also examined by TEM. Fig. 5 shows a cross-sectional HRTEM image, selected area diffraction patterns (SADP) and dark-field TEM images of the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating.

The HRTEM image (Fig. 5(a)) clearly shows that the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating was a fine composite of nanocrystallites and an amorphous phase, which could be distinguished by the lattice fringe contrast. The dark-field TEM image of the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating (Fig. 5(b)) show that fine (Ti, Si)(B, N) crystallites (white area) distributed uniformly in the matrix. XRD, XPS and HRTEM showed that the crystallites and amorphous phase were (Ti, Si)(B, N) and BN/Si₃N₄, respectively.

Mechanical properties of Ti-Si-B-N coatings

Fig. 6 shows the microhardness of the Ti-Si-B-N coatings as a function of the Si content. As the Si content, Si/(Si+B), increased, the microhardness of the Ti-Si-B-N coatings increased from ~36 GPa to ~45 GPa $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating. The improved for the microhardness seems to be mainly originated by the formation of solid-solution (Ti, Si)(B, N) crystallites and an additional Si₃N₄ amorphous phase. As shown in Fig. 2(a), the high angle shift of the XRD peak suggests compressive stress resulting from Si dissolution into the Ti (B, N) crystal lattice, which can contribute towards the increased microhardness. In addition, the Si_3N_4 that precipitated at the grain boundary would simultaneously cause grain boundary hardening through the formation of strong grain boundary cohesive energy with the amorphous BN phase, which restricts grain boundary sliding [15]. On the other hand, the microhardness decreased again to ~32 GPa for the Ti_{0.76}Si_{0.24}N coating with further increase in the



Fig. 6. Microhardness of Ti-S-B-N coatings as a function of Si content.



Fig. 7. Average friction coefficient of Ti-Si-B-N coatings as a function of Si content.

Si content after achieving the maximum microhardness, which is considered to be due to the grain size effect. As shown in Fig. 2 (b), the grain sizes increased from ~13.7 nm to ~35.9 nm with increasing Si content in the coatings. ideal interactions The between the nanocrystallites and amorphous phase can be lost when the grain size in the nanocomposite coatings increases [16]. In addition, an increase in the grain size of the Ti-Si-B-N coatings can result in the decrease of the microhardness of the coatings according to the Hall-Petch relationship [17]. The microharness of the our PECVD Ti-Si-B-N coatings (~45 GPa) was much higher than that of the PVD Ti-Si-B-N coatings (≥25 GPa) [8-9].

The friction coefficients of the PECVD Ti-Si-B-N coatings were evaluated using a steel ball (diameter

6.34 mm, 700 H_v 0.2) as a counter part material. Fig. 7 shows the average friction coefficient of the Ti-Si-B-N coatings as a function of the Si content under a normal load of 5 N at ambient temperature (~24 °C) and a relative humidity of 25~30%. In general, Ti-B-N coatings with a high B content have a relatively low friction coefficient because amorphous h-BN acts as a lubricant [18-19]. In addition, h-BN sometimes reacts with ambient H₂O to produce B₂O₃ via a tribo-chemical reaction, which acts as a self lubricant layer [20]. As the Si content, Si/ (Si+B), increased, the mean friction coefficient of the Ti-Si-B-N coatings decreased from ~0.43 to ~0.4 for the Ti_{0.74}Si_{0.04}B_{0.21}N coating. The decrease in friction coefficient at Ti_{0.74}Si_{0.04}B_{0.21}N might be caused by multi-action between h-BN and the additional self lubricant layer, such as B₂O₃, SiO₂ and Si(OH)_x [15, 20-21]. SiO₂ and Si(OH)_x play a role in forming a self lubricant layer [22]. On the other hand, the average friction coefficients increased again with further increases in Si content after achieving a minimum average friction coefficient. The increased average friction coefficient seems to be due to the decrease in amorphous h-BN volume fraction in the Ti-Si-B-N coatings.

Conclusion

Quaternary Ti-Si-B-N coatings were deposited on AISI 304 substrates by PECVD using a TiCl₄, BCl₃, SiH₄, N₂, H₂, and Ar gas mixture. Instrumental analyses revealed that the chemical vapor deposited Ti-Si-B-N coatings consisted of a solid-solution of nano-sized (Ti, Si)(B, N) crystallites and amorphous BN/Si₃N₄ phase. The Ti-Si-B-N coatings exhibited a maximum hardness of ~45 GPa for the $Ti_{0.74}Si_{0.04}B_{0.21}N$ coating due to the increase in cohesive energy at the grain boundary through the formation of amorphous Si₃N₄ as well as solid-solution hardening. The microhardness of the PECVD Ti-Si-B-N coatings was much higher than that of PVD Ti-Si-B-N coatings. In addition, the Ti_{0.74}Si_{0.04}B_{0.21}N coatings showed the lowest mean friction coefficient of 0.4 against a steel ball compared to the TiN, Ti_{0.75}B_{0.25}N, and Ti_{0.76}Si_{0.24}N coatings prepared under the same PECVD conditions.

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