# Synthesis and investigation of structural-mechanical-tribological properties of c-BN based BN thin films

**İhsan Efeoğlu[1]\*, Yaşar Totik[1], Ayşenur Keleş[1], Kıvılcım Ersoy[2], Göksel Durkaya[3]**

**[1] Ataturk University, Department of Mechanical Engineering, 25240 Erzurum, Turkey**

**[2] FNSS Defense Industry, 06830 Ankara, Turkey**

**[3] Atilim University, Department of Metallurgical and Materials Engineering, 06836 Ankara, Turkey**

## ARTICLE INFO

## ABSTRACT

c-BN films are candidate material to diamond due to their promising properties. Although some properties of c-BN films are better than diamond, adhesion properties between the substrate and the film are very poor. In this study, c-BN films were deposited by closed-field unbalanced magnetron sputtering system onto 4140 steels in $Ar/N_2$ atmosphere. The c-BN films coated in three different $N_2$ flow rates. The coated specimens were characterized by SEM and X-ray diffraction techniques. The bonding state of B, N and C elements were obtained using XPS. The mechanical properties of the c-BN films were tested by micro-indentation. The adhesion properties between substrate and the film were investigated by using scratch test. The tribological properties were carried out using pin-on-disc in atmospheric conditions. Our results showed that the c-BN films exhibited very dense and columnar microstructure. The maximum critical load was read 23 N in the softest c-BN film. The maximum and minimum hardness were measured 69 GPa and 33 GPa, respectively. When the hardness was increased the friction coefficient was decreased. The lowest friction coefficient (0.15) was obtained from the hardest film and the highest friction coefficient (0.65) was obtained from the lowest hardness.

## 1. Introduction

c-BN is one of the attractive materials due to have promising and good properties. It is the second hardest material in the universe [1]. With its properties, c-BN resembles the diamond. Moreover, some properties of c-BN is better than diamond. The atomic density of c-BN is less than 4% of diamonds. For c-BN, 1200 ºC is oxidized temperature and its graphitization temperature is around 1500 ºC. These values are 600 ºC and 1400 ºC as to the diamond. Despite a fume on the magnetic metals contact with diamond, c-BN is chemically inert. Despite its attractive properties, c-BN has very poor adhesion between substrate and the film due to compressive internal stress. For improving adhesion, first aim is to minimize this internal stress [1-3].

In literature, some scientific studies are done for minimizing internal stress in c-BN films. Ma et al. in 1998 [4] coated c-BN different substrate material using CVD for improving adhesion. They figured out that c-BN coated on Ni substrate had good adhesion. This reason is that the Ni lattice parameter value (0.352 nm) approximate the c-BN lattice parameter value (0.362 nm). In 2001, Klett et al. [5] used high ion energy and/or low $Ar/N_2$ rate for diminishing internal stress. After this research, internal stress was obtained 5GPa. Ye et al. in 2008 [6] coated c-BN using RF magnetron sputtering under 400 ºC process temperature and -250V bias voltage. They sent oxygen in plasma during process. Through, the internal stress was diminished. Ulrich et al. in 2010 [7] coated c-BN using reactive magnetron sputtering and kept constant $N_2/Ar$ concentration (1/16) in the plasma. It was noted that the optimum stress has been pointed out. Finally, Caicedo et al. in 2015 [8] grew c-BN coating by using RF magnetron sputtering. They coated $TiN[BCN/BN]_n$ bilayer before grown c-BN. They changed number (n) of BCN/BN bilayer coatings. They clarified that the critical load was increased with increasing bilayer number.

In this work, c-BN films were deposited by Closed Field Unbalanced Magnetron Sputtering (CFUBMS) system onto 4140 steels in $Ar/N_2$ atmosphere. The mechanical, structural and tribological properties of c-BN films were investigated. The results showed that c-BN films have very dense microstructure, high hardness and low friction coefficient. The critical load of c-BN film is very promising.

*corresponding author: iefeoglu@atauni.edu.tr

## 2. Materials and methods

4140 steel substrates with a diameter of 27 mm were hardened and tempered to a $HV_{0.1}= 210$ (≈2.06 GPa) and Si wafer was selected for structural analysis.The chemical composition (as wt%) of the steel is given Table 1. The 4140 steel substrates were polished to a roughness value of Ra ≈ 0.1 µm using SiC emery paper with 1200-mesh grit. After mechanical surface preparation, the polished substrate surfaces were ultrasonically cleaned with ethanol and dried, and then the substrate surfaces were etched using 2% nital solution.

**Table 1.** The chemical composition (wt%) of 4140 steel

| The substrate metal | C | Mn | Cr | Si | Mo | P | S |
|---|---|---|---|---|---|---|---|
| 4140 | 0.4 | 0.75 | 0.9 | 0.2 | 0.15 | ≤0.03 | ≤0.04 |

The c-BN films was performed by CFUBMS system by produced Teer Coating Ltd [9-10]. For depositing the c-BN films; one $B_4C$ target, one Ti target and $N_2$ reactive gas were used. Additionally, Ar gas was used for ionization. Before deposition process to eliminate contamination and improve adhesion between the substrate and the film, ion cleaning was realized in pressure 0.27 Pa for 20 minutes. For minimizing residual stress and improving adhesion before depositing, Ti and TiN interlayers were coated. The parameters of coating process were given in Table 2.

**Table 2.** The deposition parameters of c-BN film

| Deposition Parameters | | | |
|---|---|---|---|
| Number of Coating | The $N_2$ flow rate (%) | | |
| R1 | 25 | | |
| R2 | 40 | | |
| R3 | 50 | | |
| Constant Parameters | | | |
| Working Pressure (Pa) | 0.40 | | |
| Substrate Bias Voltage  (-V) | 70→80 | 80→90 | 90 |
| The Current of $B_4C$ (A) | 2 | 2.5 | 3 |
| Coating Time (min) | 5 | 10 | 10 |
| Ti | The target current:3A | | |
| TiN interlayer | The rate of Ar/$N_2$: 0.65 | Working Pressure: 0.26 Pa | |
| | | Total Time: 10 min | |

The working pressure was kept constant in 0.40 Pa. The pulsed-DC bias was applied to substrates in the system. During the process, the substrate bias voltage was gradually increased from -70 to -90 V, in 25 min. The $B_4C$ target current was gradually increased from 2 to 3 A. The $N_2$ flow rates (%) were 25, 40, and 50 for R1, R2, and R3, respectively. The deposition continued for 35 min. To minimize internal residual stress and improve adhesion between substrate and c-BN film, Ti:TiN:$B_4C$:h-BN:cBN graded-composite layer was coated on the substrate. The architecture structure of the graded coating is shown in Figure 1.
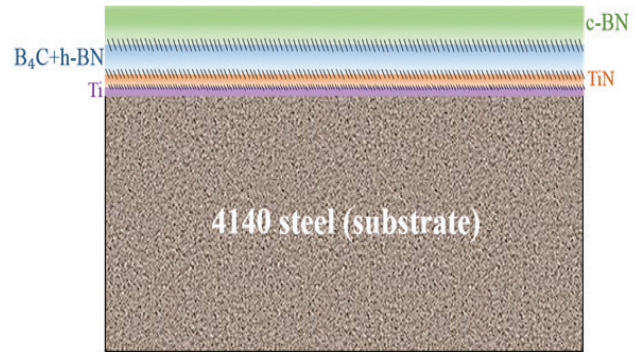


**Figure 1.** The architecture structure of c-BN film

The coating thickness, the microstructure, the stoichiometry were analyzed with JEOL-6400-SEM and energy dispersive spectrometry (EDS). The microhardness of the coatings was measured using Buehler Micromet 2001 microhardness tester (using Vickers indenter, 10gf load). The crystallographic orientation was characterized using Rigaku DMax-2200 XRD with a Cu-Kα (λ: 1.5405 Aº) radiation source (at 32º to 42º scan range). From the XRD graphics, full width half maximum (FWHM) was measured to estimate the crystallite sizes. To estimate the crystallite sizes T of c-BN, the Scherrer formula was used

$$T = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

Where λ is the copper radiation, β is the FWHM and θ is the diffraction angle. The bonding states of B, N, and C were obtained by using PHI 5000 VersaProbe XPS. To determine adhesion value of c-BN films were tested using CSM Instruments scratch tester (100 N/min progressive loading rate, 200 micron radius Rockwell-C diamond tip). The wear test under atmosphere pressure was carried out CSM high temperature tribotester (2N load, 25 ºC, %45-55RH, 10cm/s velocity, 6.25 mm diameter of $Si_3N_4$ counterpart).

## 3. Results and discussions

The microstructure and thicknesses of c-BN films were determined by SEM. For analyzing, c-BN films coated on silicon wafer was used. The SEM pictures of the cross section and the film thickness are given in Figure 2. c-BN films coated using CFUBMS had a very dense and columnar microstructure at minimum surface defect for all coatings. The thickness of the films are 2.176 µm, 1.448 µm and 0,936 µm for R1, R2 and R3, respectively. EDS results are given in Table 3. In EDS results $N_2$ content is the highest in R3. With increasing $N_2$ flow rate, the films thicknesses were decreased.

The measured microhardness values are 69 GPa, 40 GPa and 33 GPa, for R1, R2 and R3, respectively. When compared EDS results, the $N_2$ content is the lowest in the hardest film R1, while high intensity of the h-BN. In the literature, increasing nitrogen content in the chamber, soft h-BN increased in the structure.
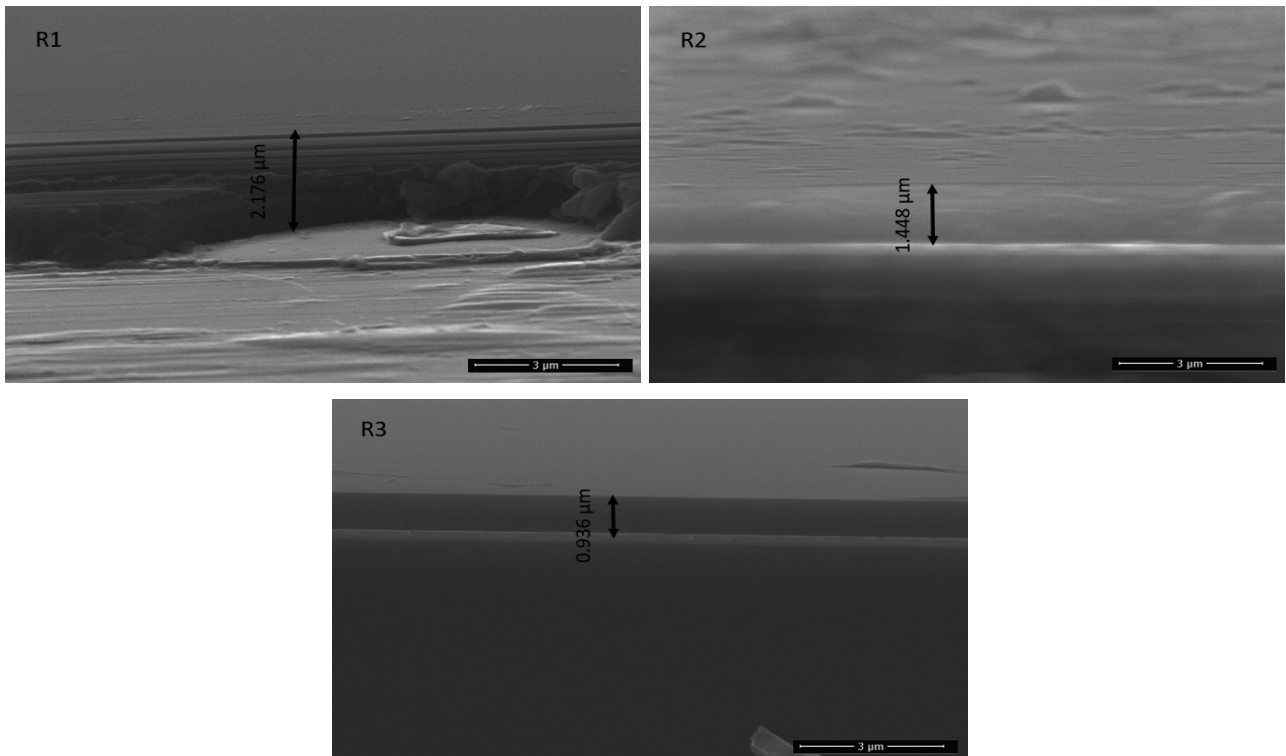
**Figure 2.** SEM pictures of c-BN films

Resulting in, the hardness decreased [10]. Normally, due to the high h-BN content, it is expected R1 film to be the lowest hardness. But $I_{c-BN}/I_{B4C}$ rate is the highest in R1 film. On the other hand, the highest content of h-BN is measured the lowest hardness from R3. Although R3 film has the highest h-BN content, its $I_{c-BN}/I_{B4C}$ rate is the lowest. It is showed that R3 film has the lowest hardness.
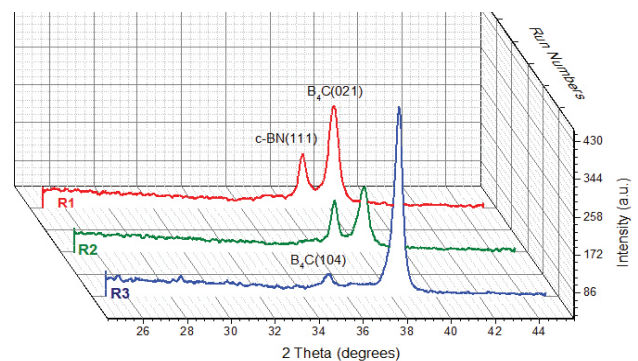
using Equation (1). The smallest crystallite size (25.4 nm) of c-BN is calculated in the hardest film and the highest crystallite size (76 nm) of c-BN is calculated in the softest film. The relation between the crystallite size and the strength is stated by Hall-Petch equation. The intensity rates ($I_{c-BN}/I_{B4C}$) of c-BN peak are calculated 0.85 for R1, 0.56 for R2 and 0.2 for R3. When the rate of intensities decreased, the hardness values decreased.
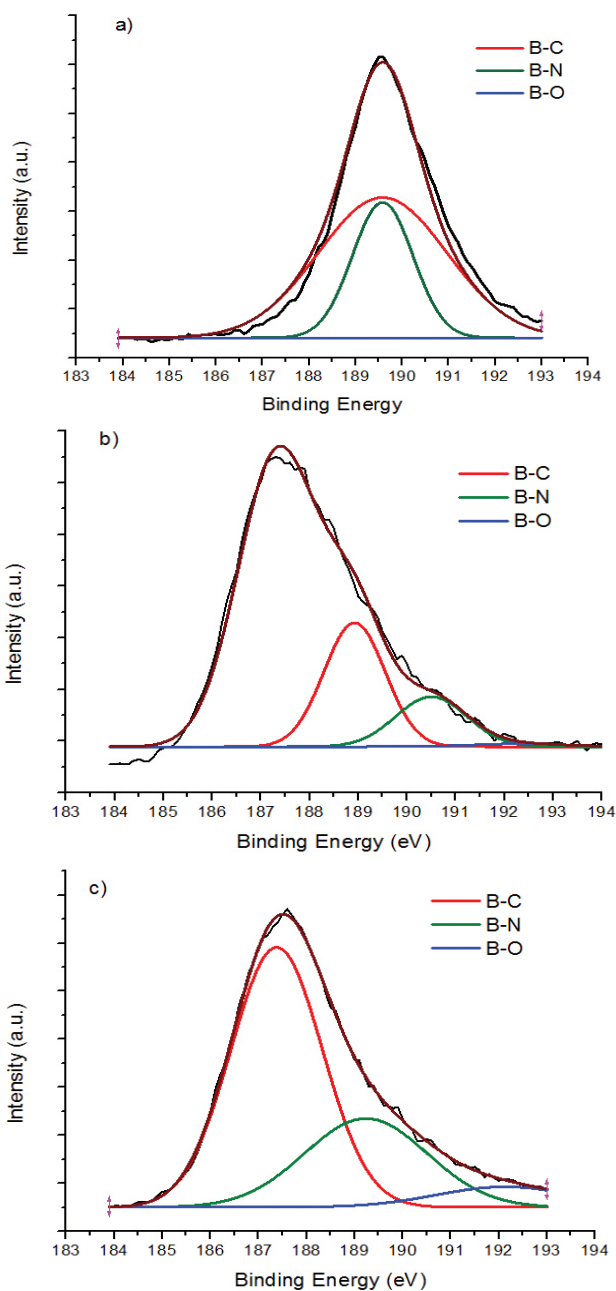
**Table 3.** EDS results of c-BN film

| Film No | R1 | R2 | R3 |
|---------|------|------|------|
| Element | | % at | |
| B-K | 43.43 | 35.86 | 38.19 |
| C-K | 27.44 | 21.29 | 11.09 |
| N-K | 27.35 | 40.93 | 48.78 |
| Ti-K | 1.78 | 1.92 | 1.94 |

The XRD patterns of c-BN films are shown in Figure 3. In all films $B_4C$ (021) peak, located at about $2\theta = 38.3°$, c-BN (111) peak, located at about $2\theta = 36.8°$ and rarely amorphous h-BN (002) peak, located at about $2\theta = 26.74°$, are found. Only in R3, $B_4C$ (104) peak, located at about $2\theta = 35.2°$, is found. When compared the c-BN (111) intensity, the minimum intensity is measured in the softest film R3. In XRD results shows that the intensity of $B_4C$ crystallites is minimum in the hardest film R1. The $B_4C$ is softer than c-BN [2]. Resulting in, the more $B_4C$ content in films are the softer films.

Table 4 shows the FWHM and the crystallite sizes (T) of c-BN in all films. The crystallite size was calculated



**Figure 3.** The XRD patterns of c-BN

**Table 4.** The crystallite size of c-BN films

| Coating Numbers | FWHM (rad) | Crystallite Size (nm) |
|-----------------|------------|-----------------------|
| R1 | 0.00576 | 25.4 |
| R2 | 0.00541 | 27 |
| R3 | 0.00192 | 76 |

According to the XPS analysis, Figure 4 shows the B 1s narrow scan for c-BN films in all coatings. The peaks between 190 eV and 190.53 eV are placed to B-N bonds [10]. The peaks 180-190 eV are assigned B-C bonds. The peak 192.42 eV can be attributed to the presence of B–O bond formed as a result of contamination [11]. The peak intensity of B-N decreases according to $N_2$ flow. When $N_2$ flow is increased, B-N content is decreased.

Figure 5 shows the N 1s narrow scan for c-BN films in all coatings. The peaks between 398.31 eV and 398.7 eV are attributed B-N bonds. The peak intensity decreases from R1 to R3. It is observed the opposite trend between B-N peak intensity and $N_2$ flow.







**Figure 5.** The XPS narrow scan of N 1s for c-BN films a) R1, b) R2, c) R3



**Figure 4.** The XPS narrow scan of B 1s for c-BN films a) R1, b) R2, c) R3

In literature, Gaitan et al. reported that the critical load of one layer $B_4C$:BCN:c-BN film was 16 N [12]. The critical load values for all films are given in Figure 6. The critical load values of c-BN films obtained with R1, R2 and R3 are approximately 17 N, 19 N and 23 N, respectively. Regarding coating process parameters, the critical load values increase with decreasing the $N_2$ flow rate. According to the literature with increasing $N_2$ frow rate, the hardnesses decrease and this decreasing hardness value diminishes compressive internal stress. Therewith, adhesion properties between film and substrate are obtained better [13-14].
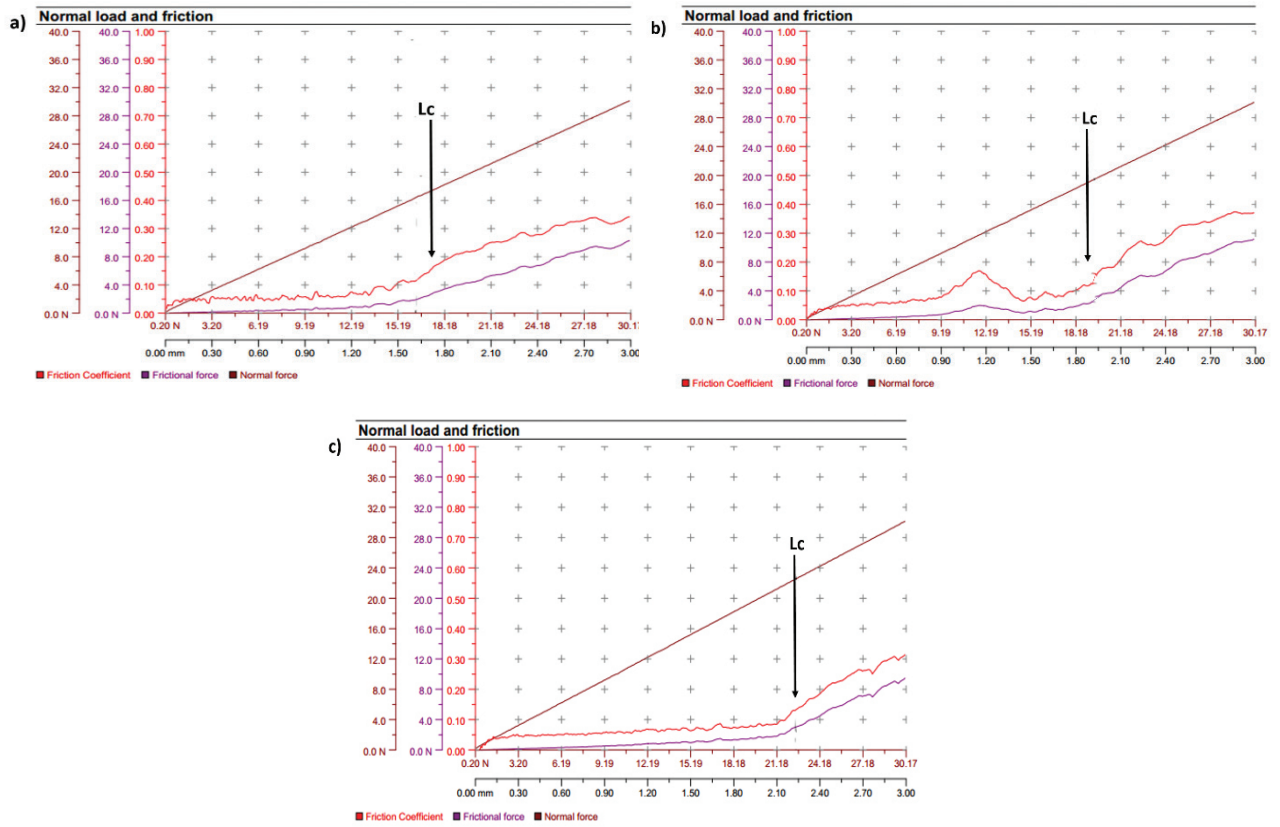
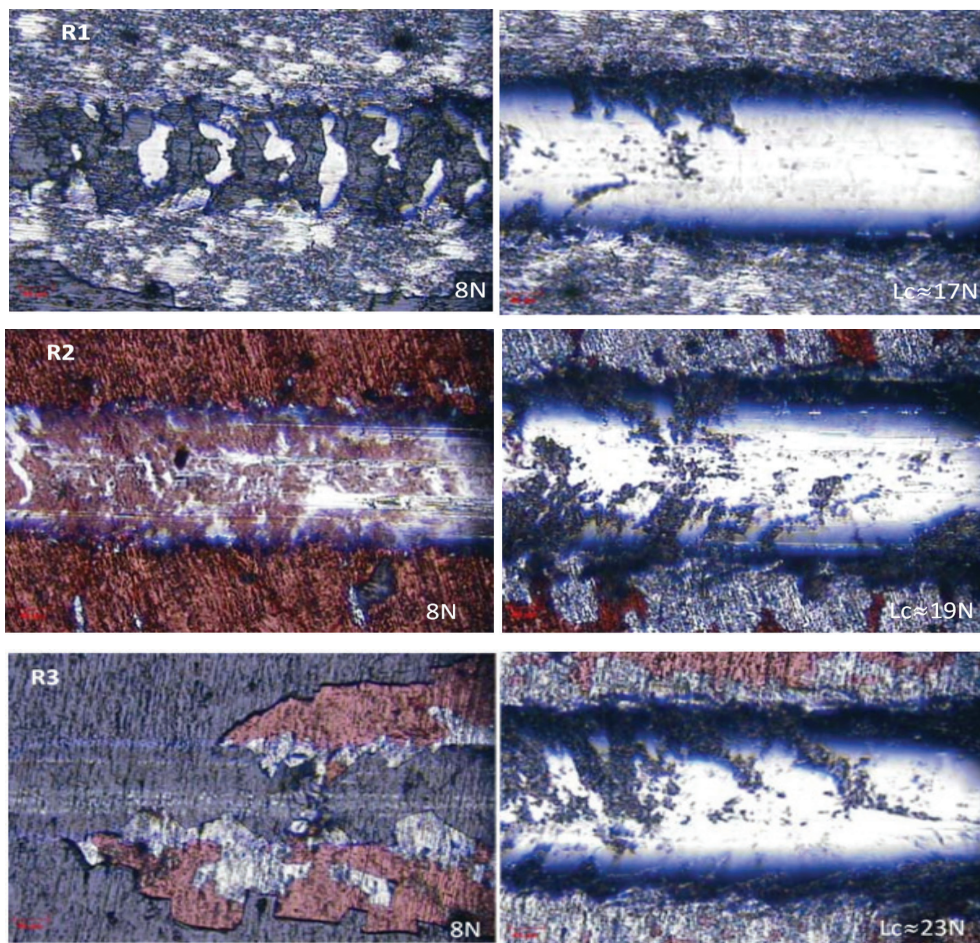**Figure 6.** The critical load values for c-BN films a) R1, b) R2, c) R3



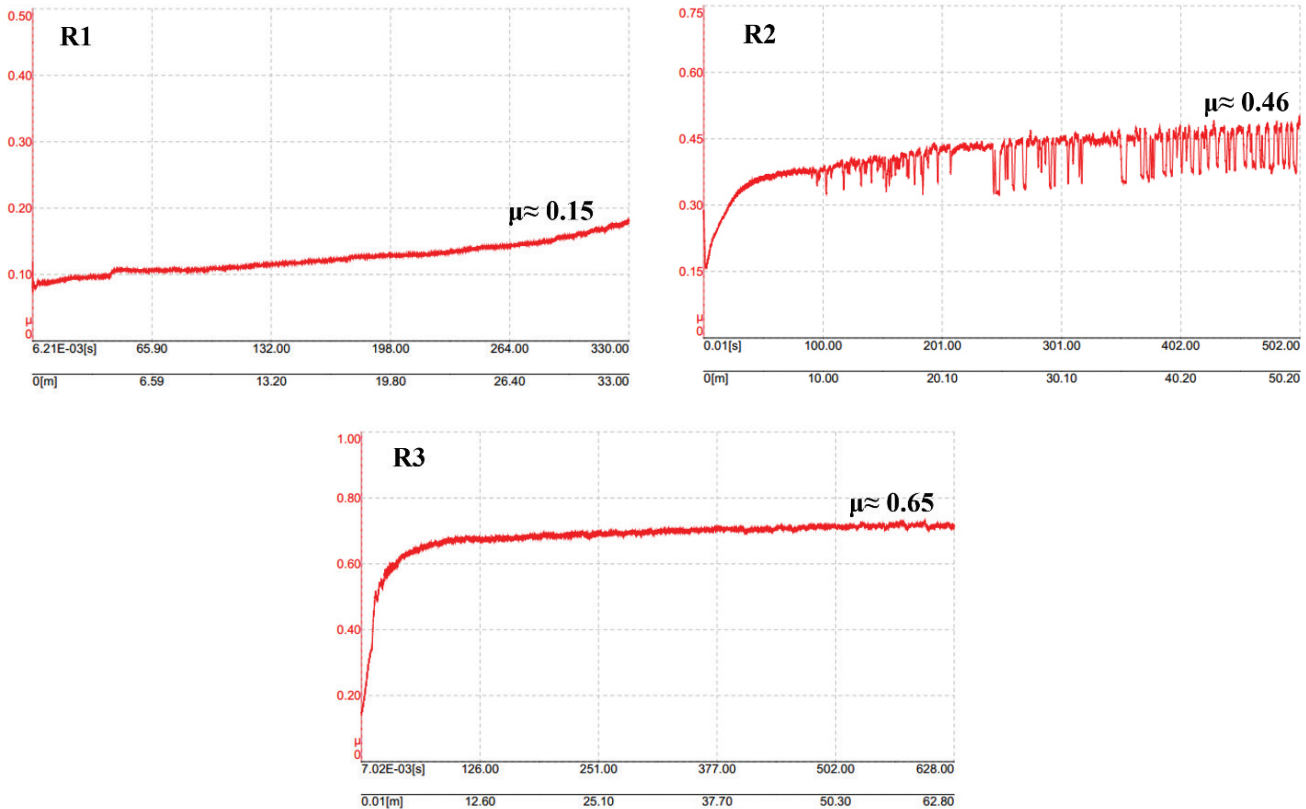**Figure 7**. Scratch tracks of c-BN films

**Figure 8.** Friction coefficient of c-BN films under atmosphere

Figure 7 shows scratch tracks for all films at 8N and their Lc load values. The all films show brittle failure at 8 N. In R1 condition, the film exhibits conformal type buckling cracks. Due to highest hardness of R1 film, the failure is obtained very brittle. In R2 condition, the chevron cracks occur. In R3 condition, the brittle side failure came out. Compared between hardness and failure, it can be said that the hardness value affects the failure type and the loss particle amount due to failure. When the hardness value of the film is increased, the failures of the film increased.

Figure 8 shows friction coefficient of c-BN films in R1, R2 and R3 conditions under atmospheric cases. Friction coefficient values of c-BN films obtained from R1, R2 and R3 conditions are 0.15, 0.46 and 0.65, respectively. As seen in Table 4, the crystallite size of R1 is the minimum value (25.4 nm). On the other hand, the crystallite size of R3 is the maximum value (76 nm). When crystallite size is compared with the friction coefficient, it is shown that the crystallite size increases with the increase of friction coefficient. It is shown that the hardest c-BN films in R1 condition shows the lowest friction coefficient. This relation, in 1950 Bowden and Tabor [15] was clarified that the friction coefficient is directly proportional with spesific friction coefficient and inversely proportional to hardness. The c-BN film in R1 condition has semi-stable friction coefficient. The friction coefficient value of c-BN film in R1 condition started with 0.1 and ended with 0.15. The c-BN

film in R2 condition has unstable friction coefficient. In the beginning, the friction coefficient begins at 0.2 and then the friction coefficient increased till at 0.46. This is because the adhesive bonding occurs between film and the counterpart. With rotating speed, the adhesive bonding rupture and it is caused the abrasive wear with increasing the friction coefficient. After 100 seconds, there is unstable the friction coefficient. It is showed that the films cracks cause the unstable friction coefficient. The c-BN film in R3 condition the friction coefficient shows two stage. In the first stage, the friction coefficient increases due to adhesive bonding rupture. This rupturing bonding causes abrasive wear. Resulting in, the friction coefficient increases. In the second stage, the friction coefficient is stable.

## 4. Conclusion

The c-BN films were deposited by CFUBMS in different $N_2$ flow rate. The c-BN films exhibited very dense and columnar microstructure. The maximum film thickness and highest hardness for the films were obtained as 2.176 μm and 69 GPa, respectively, in the lowest $N_2$ flow rate. According to XRD results, $B_4C$ (021) crystallite, c-BN (111) crystallite and h-BN (002) crystallite were grown in all films. Only in R3, $B_4C$ (104) crystallite was grown with $B_4C$ (021) and c-BN (111) crystallites. XRD results showed that the intensity of $B_4C$ crystallites is minimum and intensity of c-BN crystallite is maximum in the hardest film R1. The smallest

crystallite size (25.4 nm) of c-BN was calculated in the hardest film and the highest crystallite size of c-BN was calculated in the softest film. According to XPS results; B-N, B-C and B-O bonds were obtained in c-BN films. The content of B-N was maximum in the hardest film R1. The maximum critical load was obtained as 23 N in the softest film R3. Regarding film parameters, the critical load values increased with decreasing the $N_2$ flow rate. The friction coefficient was obtained minimum as 0.15 in R1.

## Acknowledgement

## References

[1]    Audronis M., Valiulis A. V., Silickas P., Recent Developments in the Deposition of c-BN Coatings, Mater. Sci. (Medziagotyra), 10, 152-156, 2004.

[2]    Jimenez I., Torres R., Caretti I., Gago R., Albella J. M., A review of monolithic and multilayer coatings within the boron-carbon-nitrogen system by ion-beam-assisted deposition, J. Mater. Res., 27, 743-764, 2012.

[3]    Zhang W. J., Chong Y. M., Bello I., Lee S. T., Nucleation, growth and characterization of cubic boron nitride (cBN) films, J. Phys. D: Appl. Phys., 40, 6159-6174, 2007.

[4]    Ma X. Y., Yue J. S., He D. Y., Chen G. G., Characterization of cubic boron nitride thin films grown on different substrates, Mater. Lett., 36, 206-209, 1998.

[5]    Klett A., Freudenstein R., Kulisch W., Dependence of the stress of c-BN films on the major deposition parameters: Theoretical and experimental studies, Thin Solid Films, 398, 130-136, 2001.

[6]    Ye J., Ulrich S., Zlebert C., Stuber M., Stress reduction of cubic boron nitride films by oxygen addition, Thin Solid Films, 517, 1151-1155, 2008.

[7]    Ulrich S., Ye J. A., Stuber M., Influence of Ar-N-2 gas composition on the magnetron-sputter deposition of cubic boron nitride films, Surf. Coat. Technol., 205, S96-S98,  2010.

[8]    Caicedo J. C., Caicedo H. H., Aperador W., TiN BCN/BN (n)/c-BN system improves the surface properties of machining tools used in industrial applications, Int. J. Adv. Manuf. Technol., 77, 819-830, 2015.

[9]    Teer D. G., Magnetron Sputter Ion Plating, U.S. Patent, 5,556,519, 1996.

[10]  Cicek H., Baran O., Demirci E. E., Tahmasebian M., Totik Y., Efeoglu I., The effect of nitrogen flow rate on TiBN coatings deposited on cold work tool steel, J. Adhes. Sci. Technol., 28, 1140-1148, 2014.

[11]  Fan X. H., Guo X. F., Xu B., ZhanG W., Cai L. C., X-ray photoelectron spectroscopy research on superficial layer of cubic boron nitride crystals grown under HPHT High Temperatures-High Pressures, 44, 407-414, 2015.

[12]  Gaitan G. B., Caicedo J. C., Prieto P., Balogh A. G., Cutting tool performance enhancement by using a B4C/BCN/C-BN multilayer system, Phys. Status Solidi C,  11, 4282-4287, 2007.

[13]  Prakash A., Todi V., Sundaram K. B., Ross L., Xu G., French M., Henry P., King S. W., Investigation of the dielectric and mechanical properties for magnetron sputtered BCN thin films, ECS J. Solid State Sci. Technol., 4, N3122-N3126, 2014.

[14]  Kiryukhantsev-Korneev P. V., Pierson J. F., Kuptsov K. A., Shtansky D. V, Hard Cr–Al–Si–B–(N) coatings deposited by reactive and non-reactive magnetron sputtering of CrAlSiB target Appl. Surf. Sci., 314, 104-111, 2014.

[15]  Bowden F. P., Tabor D., The Friction and Lubricating of Solids, Oxford University  Press, New York, 1950.