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Research Article

Effect of deposition parameters on structural and mechanical properties of Novel h-BN doped TiCrNbN coatings

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Abstract

In this paper, the novel h-BN doped TiCrNbN thin films was deposited on the DIN 1.2714 steel using closed field unbalanced magnetron sputtering (CFUBMS) technique with variable working pressure, bias voltage, and LaB6 target voltage. The main goal is to determine the contribution of degrees of these parameters on structural and mechanical properties using Analysis of Variance (ANOVA). The deposition parameters were leveled based on L9 (33) orthogonal Taguchi design method. Microstructural and thickness of coatings were investigated using SEM. The coatings had granular and flawless surface properties. The thickness of the coatings was determined in the range of 874 nm and 1.69 µm. The deposition parameter that has the highest contribution to coating thickness is working pressure. Hardness and adhesion strength of coatings were determined employing nanohardness and scratch tester, respectively. The highest hardness among the coatings was 24.67 GPa, obtained with the 3x10-3 Torr working pressure, 100 V bias voltage and 600 V LaB6 target voltage parameters. The deposition parameter that has the highest contribution to hardness is working pressure. The coating conditions with the highest hardness exhibited the highest adhesion strength. The superiority of the contribution of working pressure on the adhesion strength was prominent compared to other parameters.

Keywords: CFUBMS, Taguchi, ANOVA, nanohardness, adhesion

Biriktirme Parametrelerinin Yenilikçi h-BN Katkılı TiCrNbN Kaplamaların Yapısal ve Mekanik Özelliklerine Etkisi

Öz

Bu çalışmada, özgün h-BN katkılı TiCrNbN ince filmler, değişken çalışma basıncı, bias gerilimi ve LaB_6 hedef gerilimi ile kapalı alan dengesiz manyetik alanda sıçratma tekniği kullanılarak DIN 1.2714 çelik yüzeyine kaplanmıştır. Çalışmanın motivasyonu, bu değişken parametrelerin, kaplamaların yapısal ve mekanik özelliklerine etki derecelerinin Varyans analizi (ANOVA) kullanılarak belirlenmesidir. Kaplama parametreleri Taguchi L9 (3^3) ortogonal dizin kullanılarak belirlendi. Kaplamaların mikroyapısı ve kesitleri SEM kullanılarak incelendi. Kaplamalar taneli ve kusursuz şekilde üretildi. Kaplamaların kalınlıkları 874 nm ile 1,69 µm aralığında belirlendi. Kaplama kalınlığına en yüksek etki derecesini sağlayan kaplama parametresinin çalışma basıncı olduğu tespit edildi. Kaplamaların sertliği ve taban malzemeye yapışma dayanımları sırasıyla nanosertlik ve çizik test cihazları kullanılarak gözlemlendi. En yüksek sertlik değeri, $3x10^{-3}$ Torr çalışma basıncı, 100 V bias gerilimi ve 600 V LaB_6 hedef gerilimi parametreleriyle üretilen kaplamada 24,67 GPa olarak elde edildi. Sertliğe en yüksek katkısı olan parametre çalışma basıncı olduğu tespit edildi. En yüksek sertliğe sahip kaplama koşulları aynı zamanda en yüksek adezyon dayanımı performansını da sergiledi. Çalışma basıncının yapışma dayanımına katkısının diğer parametrelere göre üstünlüğü ön plana çıkmıştır.

Anahtar Kelimeler: CFUBMS, Taguchi, ANOVA, nanosertlik, yapışma

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1. Introduction

Increasing the hardness and mechanical performance of tools employed in industry is essential for market competition in today's industrial conditions [1]. In the studies carried out in this context, surface coatings produced under vacuum have come to the fore due to magnificent features such as high hardness and wear performance [2]. Physical vapor deposition (PVD), chemical vapor deposition (CVD), sol-gel, micro-arc oxidation, anodization, thermal spray, etc. have been performed for this goal over the years [3]. Closed field unbalanced magnetron sputtering (CFUBMS) technique is commonly used owing to high homogeneity, adhesion, and usability for variety of substrate materials [4]. Nitride-based thin hard coatings performed with this PVD technique are capable of meeting the needs in the industry [5]. It is known that the mechanical properties of coatings depend on the structural properties that occur during the deposition process. The structural properties of thin films are depending on some deposition parameters such as bias voltage, working pressure, target current or/and voltage, the distance between target and substrate, frequency, and duty time. Since these parameters constantly interact with each other, each combination of them creates a unique structure. In investigating the effects of parameters on the properties of coatings, it is commonly used to keep one variable and the others constant [6]. However, in this technique, long operating time and high costs are encountered to obtain optimum coating properties. In order to overcome this difficulty, the design of experimental (DOE) methods that enable the optimization of complex processes is developed [7]. Among these methods, Taguchi is the most widely used. In the Taguchi method, the findings obtained from the tests of thin films produced by changing multiple parameters simultaneously are analyzed by Signal/Noise (S/N) ratio. Whether any parameter contributes to the coatings is evaluated with the data determined from the S/N graphs. Some studies in the open literature have tried to explain the effects of deposition parameters on coating properties. However, there are rare studies in which the contribution percentages of parameters to properties are examined numerically.

In this study, h-BN doped TiCrNbN coating was deposited to improve the mechanical properties of 1.2714 steel, which is frequently used as a die material in the industry. L9 (3^3) orthogonal design is used for experimental design. The variable parameters are working pressure, bias voltage, and LaB6 target voltage and these variable parameters are leveled at 3 different values. Structural properties and cross-sections of the coatings were examined by scanning electron microscope (SEM). The hardness and adhesion strength of the samples were determined by nanohardness and scratch tests, respectively.

2. Material and Methods

The h-BN doped TiCrNbN coatings were deposited on DIN 1.2714 (C~0.56, Cr~1.1, Mo~0.5, Ni~1.7, V~0.1, and balance Fe) using closed field unbalanced magnetron sputtering in a Teer Coating Ltd. UDP550 system under variable deposition parameters, based on a Taguchi L9 orthogonal design. Deposition parameters are shown in Table 1. Figure 1 shows the magnetron configuration of the targets to deposit the films. Before the deposition, the surfaces of the steel samples were grinded and polished. Afterwards, the ultrasonically cleaned samples are ready for deposition process. In the deposition process, one Ti (%99.95 pure), one Cr (%99.95 pure), one Nb (%99.95 pure), and one LaB6 (%99.95 pure) targets were employed to deposit planned thin films. As seen in Figure 1, the substrates were positioned 70 mm away from the targets within the means of the mechanism. After the samples were placed in the system, ion cleaning was performed on the substrates for 30 minutes in an argon atmosphere to remove any contamination on the surfaces. Afterwards, Cr interlayer was deposited on the steel surface at 10 min. for increasing the adhesion of film. CrN layers for 10 minutes, TiCrN for 20 minutes, TiCrNbN for 20 minutes and TiCrNb-hBN layers for 30 minutes were gradually coated on the samples. The microstructures of the coatings were investigated by scanning electron microscope (SEM), EDS (Energy-dispersive spectroscopy) and XRD (X-Ray diffractometer), respectively. Microscale hardness tests are not suitable for determining hardness values in thin film applications. In order to minimize the effect of the substrate, the hardness of the samples was determined by nano hardness test. The nano-hardness of the coatings was explored by a Bruker Hysitron Ti950 nanohardness tester (using Berkovich indenter, 1 mn load at 5 different points). The bond strength between thin films and substrate were determined using the scratch tester (CSM Revetest RST) having a 200 μm diameter of Rockwell-C diamond pin. A Ducom tribotester (5N load, 150 rpm rotation speed, 6 mm diameter Al_2O_3 abrader) was employed to investigate the wear behavior of samples. The wear volumes of samples were determined by optical profilometer. The wear mechanisms of samples were characterized by SEM.

Table 1. Deposition parameters

Coating No	Working Pressure (Torr) ($x10^{-3}$)	Bias Voltage (V)	LaB6 Taget Voltage (V)
R1	2	50	600
R2	2	100	700
R3	2	150	800
R4	2.5	50	700
R5	2.5	100	800
R6	2.5	150	600
R7	3	50	800
R8	3	100	700
R9	3	150	600

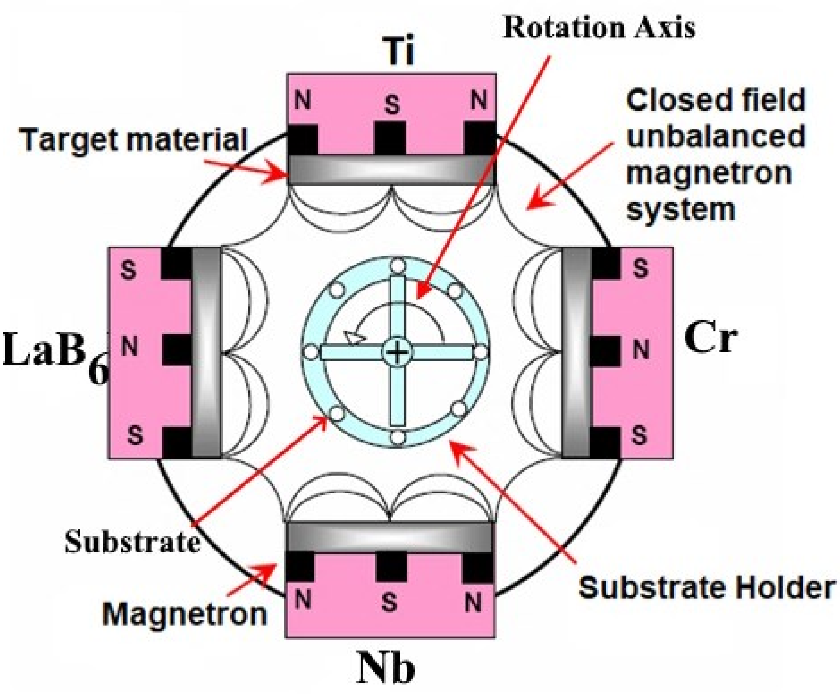
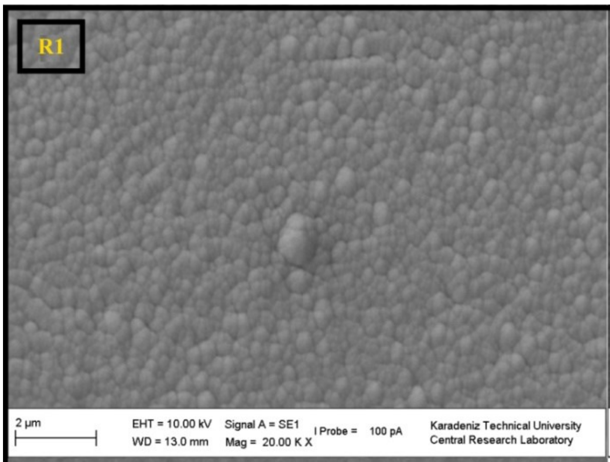


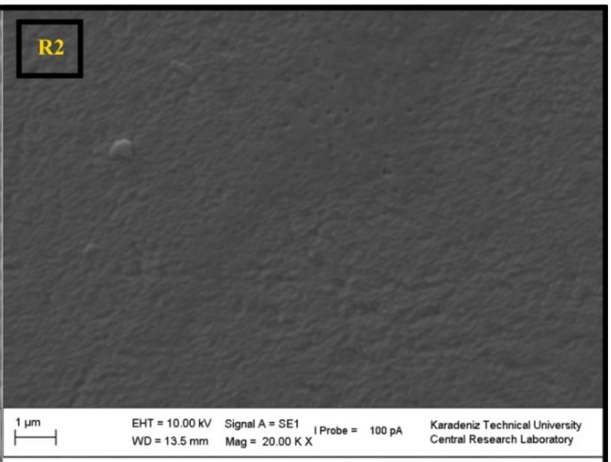
Figure 1. Magnetron sputtering system

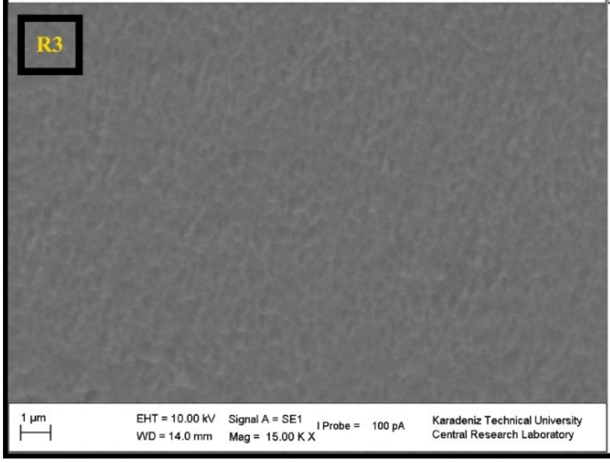
3. Results and Discussion

Surface SEM images and chemical compositions of TiCrNb-hBN thin films are given in Figure 2. As can be seen from the Figure 2, the coatings deposited on the DIN 1.2714 surface with the deposition parameters in Table 1 generally have a granular, smooth (without deposition defects) and dense structure. These flawless surface features are achieved by the high power density close field magnetron sputtering method. In this method, a closed magnetic field created by the targets traps the sputtered atoms in the plasma and delivers them directly on the substrates. When the first group (R1, R2 and R3) is examined, it is observed that a denser and fine-grained structure is obtained as the bias voltage increases. The coarse grained structure seen in the R1 coating is due to the low mobility of the sputtered atoms absorbed on the surface [8]. It is evaluated that by increasing the bias voltage value and LaB6 target voltage from 50 V and 600 V to 150 V and 800 V, adatom (adsorbed atom) mobility increases, which enhances the nucleation areas and reduces the grain size. It is obvious that the grain size decreases by increasing the bias voltage during coating processes, which is compatible with various studies in the literature [9]. It is stated that the atoms with increased energy in the plasma diffusely fill the gaps between the grains of the substrate. It is seen that as the LaB6 target voltage is increased (600 V to 800 V), the microstructure changes from a granular to a fibrous. It is determined that the fibrous structure seen in the R3 coating belongs to the “T region” in the coating structure model specified by Thornton [10]. In the elemental analysis of the coatings, it is seen that Cr is dominant in the structure. The reason for this is based on the deposition of Cr and CrN as an interlayer on the substrate. It is also known that one of the most important factors affecting the chemical composition of coatings is sputtering efficiency. This phenomenon is expressed as the amount of atoms sputtered from the target surfaces during the deposition process. In this thin film, the element with the highest sputtering efficiency (1.18) among the target materials is Cr. However, at 150V bias voltage, there is a slight decrease in the boron content due to the re-sputtering effect. Among the elements in the structure, the atomic weight of boron is lighter than other elements. Therefore, by increasing the bias voltage above 100 V, atoms with high kinetic energy cause the lighter boron atoms to re-sputter.

Similar evaluations can be made for R7, R8 and R9 coatings, where the working pressure is kept constant at 3x10-3 Torr. It is seen that the R9 coating produced at 150 V bias voltage has cauliflower-like grains. A compact and fine-grained structure is observed in the R8 coating deposited with 100 V bias voltage and 600 V target voltage.

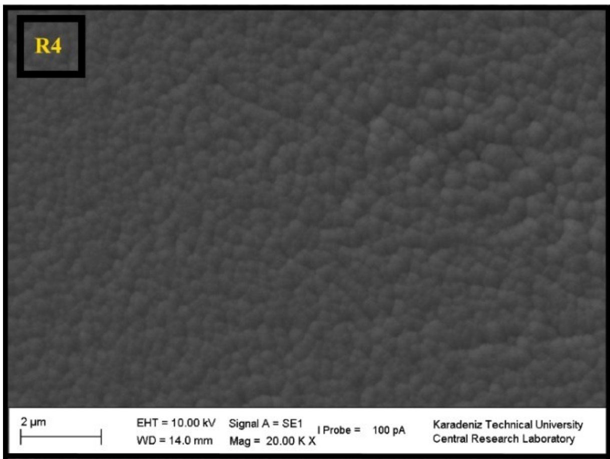


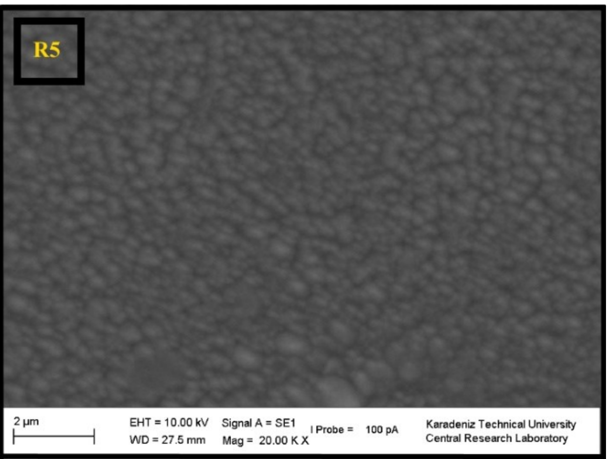


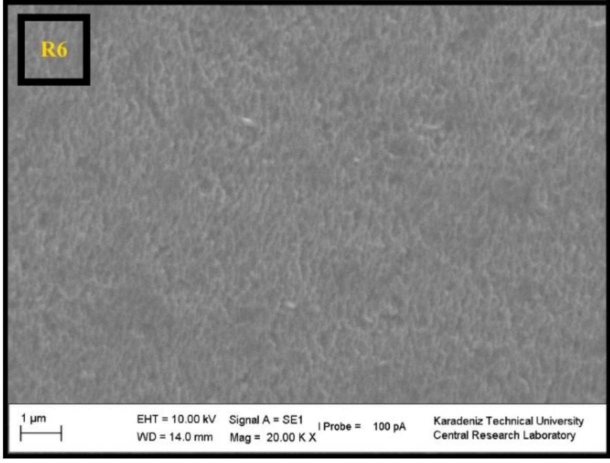


Chemical Composition of Coatings (wt%)

Coating No	Ti	Cr	Nb	B	N
R1	22.75	30.67	1.34	12.7	32.54
R2	22.44	30.39	1.62	14.33	31.12
R3	18.32	30.15	1.46	11.37	28.13

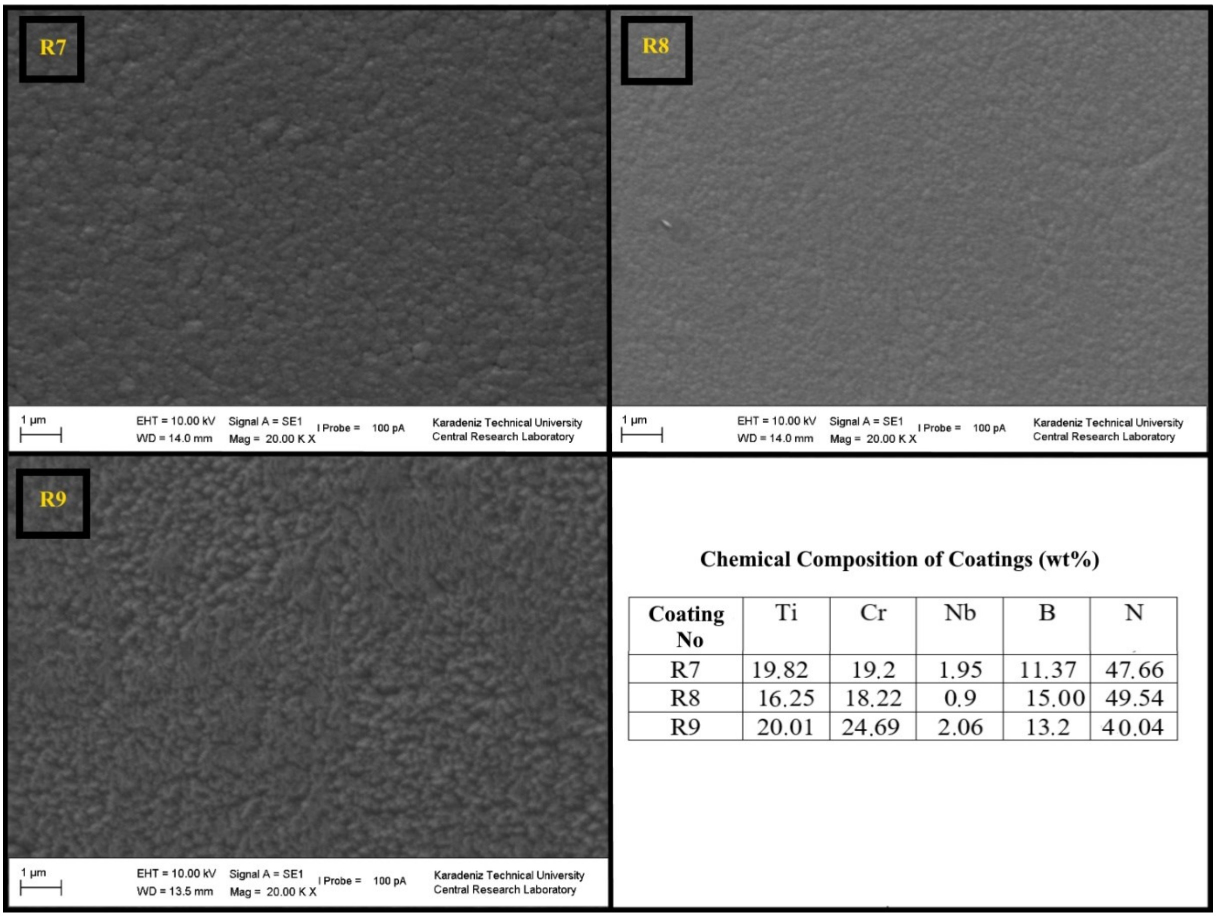






Chemical Composition of Coatings (wt%)

Coating No	Ti	Cr	Nb	B	N
R4	22.94	29.71	1.82	12.78	32.75
R5	23.00	29.52	1.89	13.16	32.21
R6	23.77	29.76	1.90	12.46	32.11



Chemical Composition of Coatings (wt%)

Coating No	Ti	Cr	Nb	B	N
R7	19.82	19.2	1.95	11.37	47.66
R8	16.25	18.22	0.9	15.00	49.54
R9	20.01	24.69	2.06	13.2	40.04

Figure 2. SEM images and chemical compositions of the coatings

Cross-sectional images of R1, R4 and R7 Coatings are given in Figure 3. It is seen that the TiCrNb-hBN layer grows in a columnar structure from the bottom layer to the surface in each of the variable parameters and there are no cracks or gaps between the grains. The thickness values obtained from these images can be seen comparatively in Figure 4. The highest coating thickness is 1.69 at R2 ($2x10^{-3}$ Torr, 100 V bias voltage, and 700 V LaB_6 target voltage). In the statistical study carried out to determine the effects of deposition parameters on the thickness of the coatings, the signal to noise (S/N) ratio is used to determine the degree of contribution of the parameters. S/N ratios of coating thicknesses are determined using Minitab 17 Software, based on the higher-the better criterion. The average S/N chart obtained as a result of the statistical analysis is given in Figure 5. As seen in Figure 5, the parameter that has the greatest contribution (63.65%) on the thickness is the working pressure. The parameter with the lowest contribution is the LaB6 target voltage (8.36%). Evaluations on coating thicknesses are carried out based on the working pressure which has the dominant contribution percentage. Increasing working pressure enhances the probability of the sputtered atoms colliding with the gas particles in the plasma during their movement to the substrate surface, causing a decrease in the deposition rate [11]. This is also one of the main reasons for the decrease in coating thickness.

There is generally a decrease in coating thickness with increasing bias voltage. This is based on the "re-sputtering" mechanism that occur when the substrate is exposed to higher intensity ion bombardment with increasing bias voltage. Studies in the literature are obtained findings consistent with this situation [12].

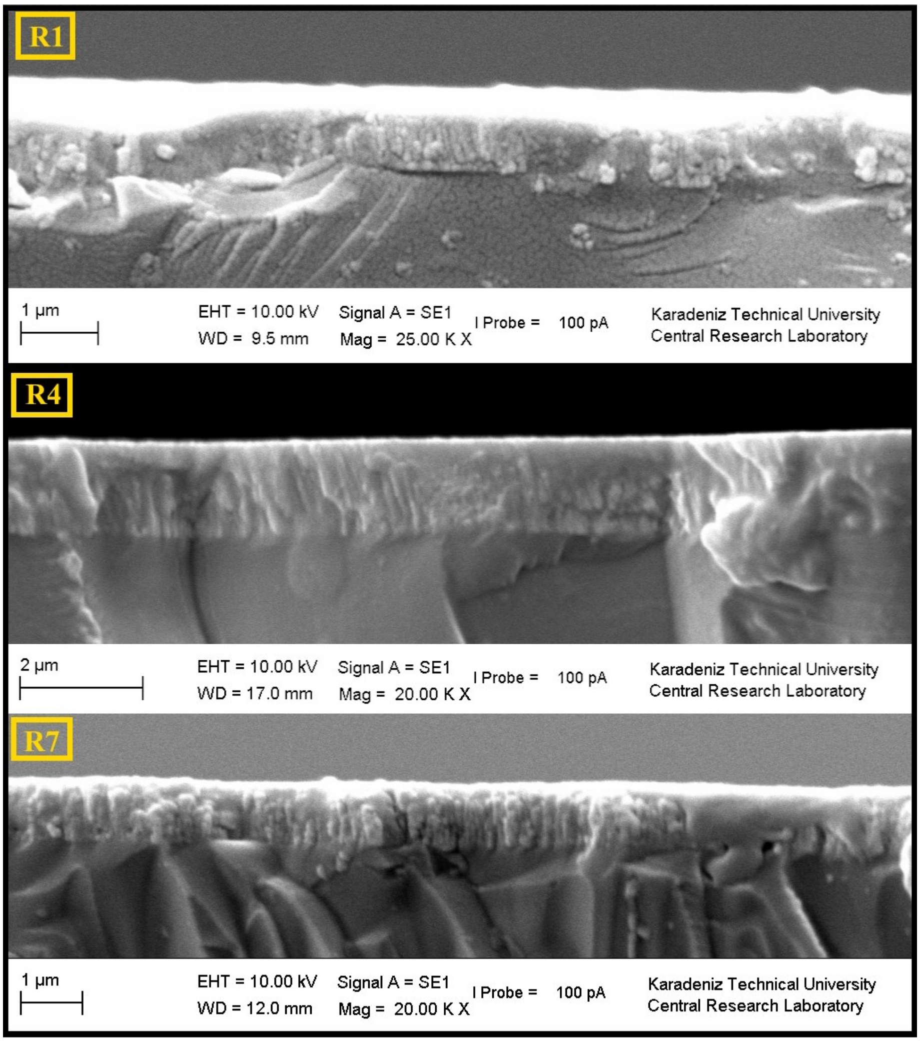


Figure 3. Typical cross-sectional SEM images of R1, R4 and R7 coatings

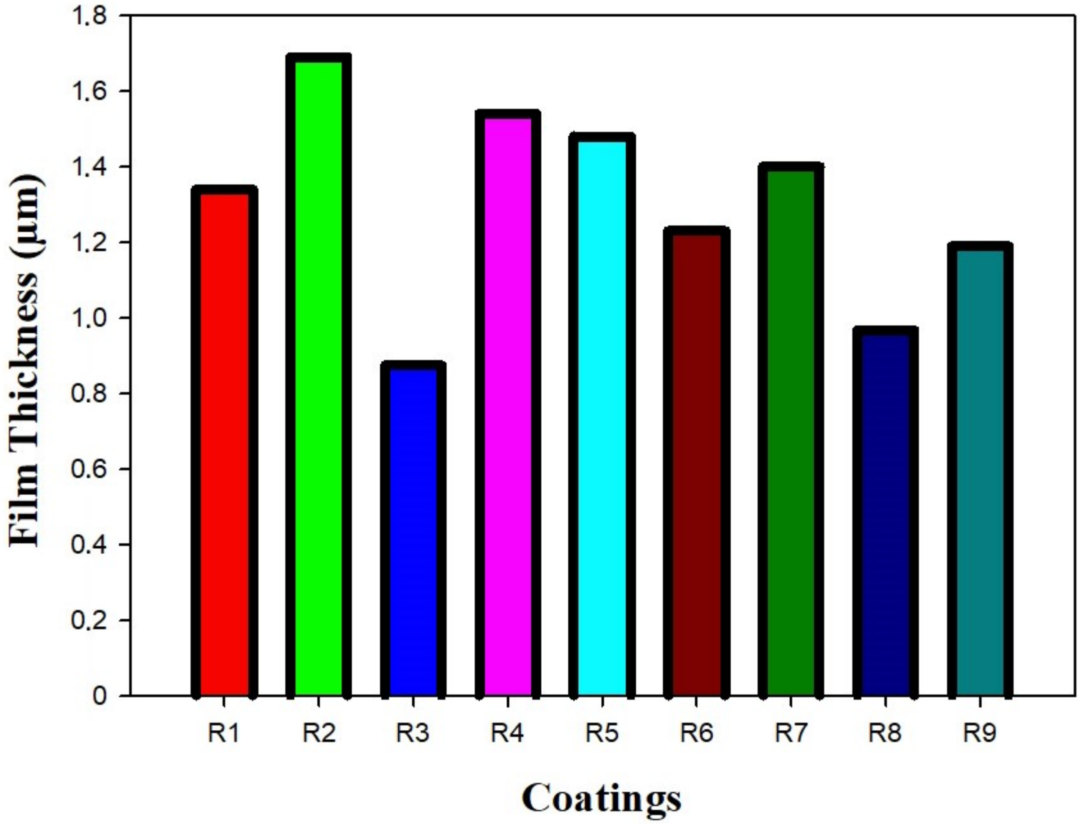


Figure 4. Thickness value of coatings

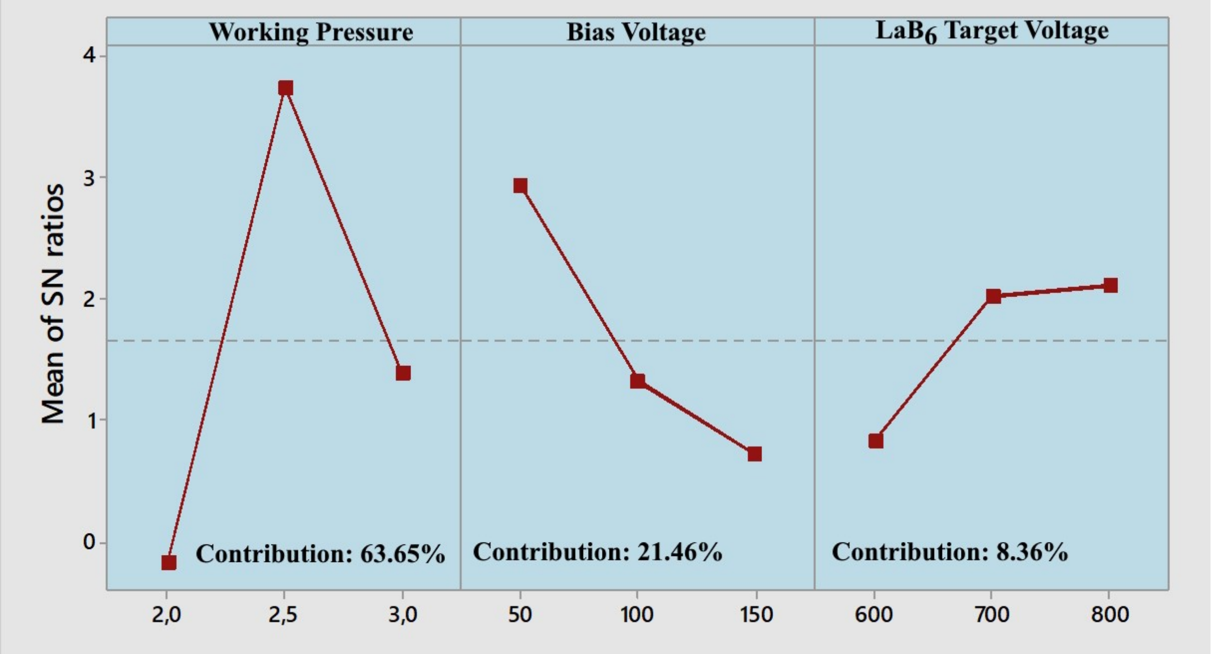


Figure 5. Average S/N Ratios for TiCrNb-hBN thin films in thickness

It is not appropriate to determine the hardness values using the microhardness test in films with coating thickness in the range of 1.00-2.00 µm. In hardness measurement, if the tip penetrates more than 20-30% of the coating thickness, this indicates that the substrate has an effect on the hardness value of coatings. Therefore, hardness measurements are carried out using nanohardness tests. The average hardness values obtained in the nanohardness test are given comparatively in Figure 6. As can be seen from the figure, the highest nanohardness value is obtained from the coating called R8 ($3x10^{-3}$ Torr working pressure, 100 V bias voltage, 600 V LaB_6 target voltage). It is determined that the hardness value of R8 is approximately 400% superior than the hardness of the 1.2714 tool steel used as the substrate. The average S/N chart obtained as a result of the statistical analysis for nanohardness values is given in Figure 7. As a result of the analysis, the parameter that has the highest contribution to the hardness values of the coatings is the working pressure (65%), while the one that has the least contribution is the LaB_6 target voltage (1%). It is determined that the nanohardness values of the R1, R6 and R8 coatings, where the LaB_6 target voltage is kept constant at 600 V, increases the working pressure increases. The highest hardness in this group is obtained as 24.67 GPa in the R8 coating produces at $3x10^{-3}$ Torr working pressure and 100 V bias voltage values. When the bias voltage was increases to 150 V, it causes a certain amount of decrease. The increase in hardness that occurs with increasing working pressure value is attributed by the enhancing ion density in the plasma. As the working pressure increases, the ion density level in the plasma increases. Thus, the substrate surface is bombarded with more atoms and a dense and tightly ordered structure is obtained. Many studies in the literature have reported findings that hardness values increase with increasing working pressure [13]. Increasing ion bombardment by increasing the bias voltage value creates preferential regions on the surface of the substrate and enhances the re-nucleation rate. In addition, the kinetic energies of the primary ions sputtered from the target also increase. Ions with high kinetic energy are directed to the substrate more quickly in the plasma, minimizing the formation of dislocations in the deposited coating layer. While these effects are present when the bias voltage is increased from 50 V to 100 V, a negative effect occurs on the hardness value at 150 V. The reason for this is that when the ions, whose velocities increase excessively, hit the surface of the substrate with a force higher than the optimum value at low working pressure levels, they cause the secondary atoms to re-sputtering from the surface.

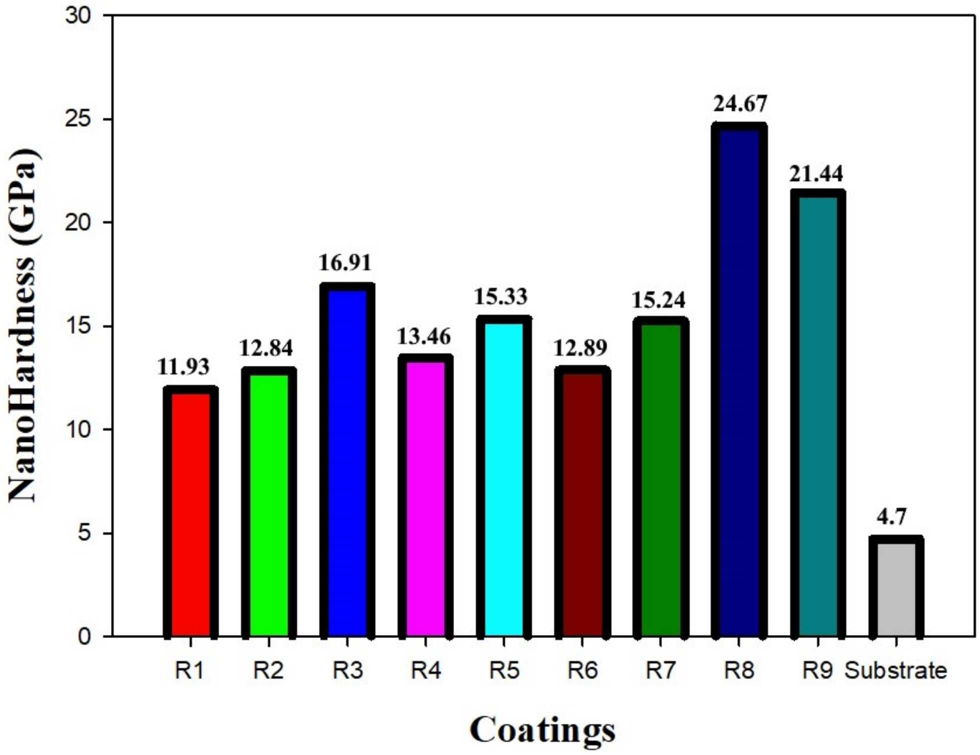


Figure 6. Average nanohardness values of samples

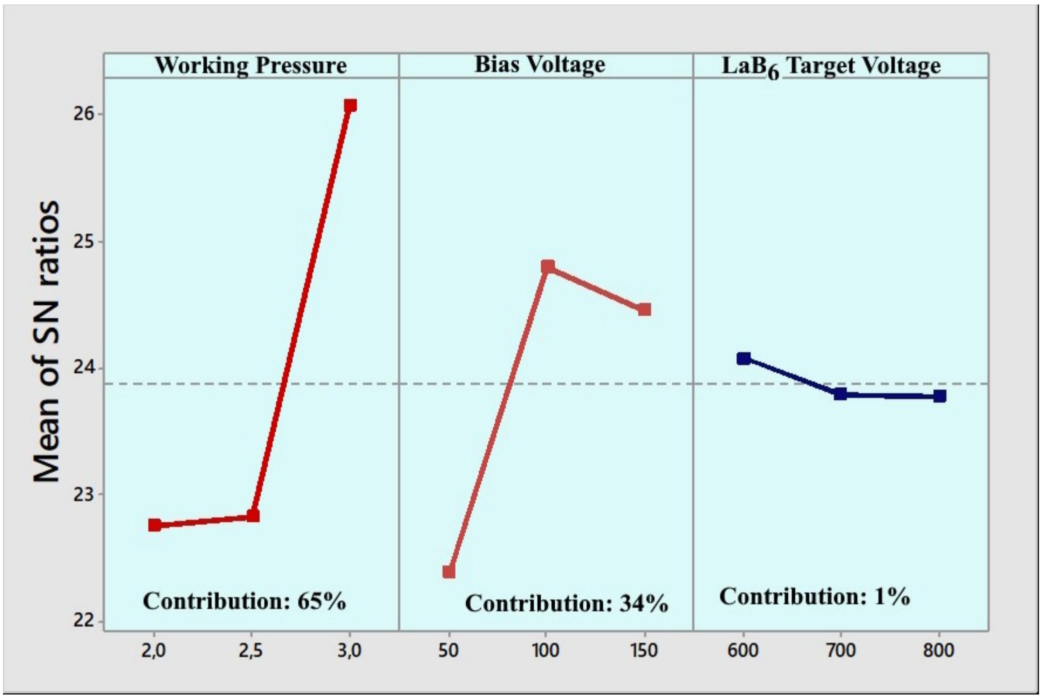


Figure 7. Average S/N Ratios for TiCrNb-hBN thin films in hardness value

The adhesion strength of TiCrNb-hBN coatings is determined by scratch test. Scratch testing is one of the most important techniques used in the characterization and performance determination of thin and hard coatings. The adhesion strength of coatings is evaluated using critical loads at which failure occurs during the test. Lc_2 critical load value is expressed as the load value at which the coating completely peels off from the substrate and loses its protection. Lc_2 critical load values of the coatings are given in Figure 8. Among the coatings, the highest Lc_2 critical load (adhesion strength) value is obtained from the R8 with 85 N, while the lowest Lc_2 critical load is obtained from the R6 with 13 N. Critical loads are determined by the normal force-friction coefficient graphs given in Figures 9, obtained using an optical microscope and optical profilometer taken from the coatings after the test. Typical scratch results for R1, R4 and R7 coatings are given for each group. S/N ratios of adhesion strength values (Figure 10) are calculated according to the higher the better criterion. It is determined that the most important parameter affecting the adhesion strength values obtained from coatings is the working pressure (89.6%). As in other properties, the lowest contribution is taken from LaB6 (1.6%). In the R1, R6 and R8 coatings, where the LaB_6 target voltage is kept constant at 600 V, which has the lowest contribution on the adhesion strength values of the coatings at 1.6%, a superior adhesion strength of 85 N is obtained in the R8 coating produced with the highest working pressure ($3x10^{-3}$ Torr). As stated before, as the working pressure increases, the ionization in the plasma increases. This has positive effects on the coating's resistance to plastic deformation and adhesion. By increasing the bias voltage from 50V to 100V in the R8, the adhesion strength of the coating increases as the ions with increases kinetic energy penetrates the surface better and forms a dense structure. In addition, increasing the bias voltage from 50 V to 100 V causes a relief in the lattice structure by reducing the residual stresses. This relief is thought to increase the load-bearing capacity of the coating by increasing its toughness.

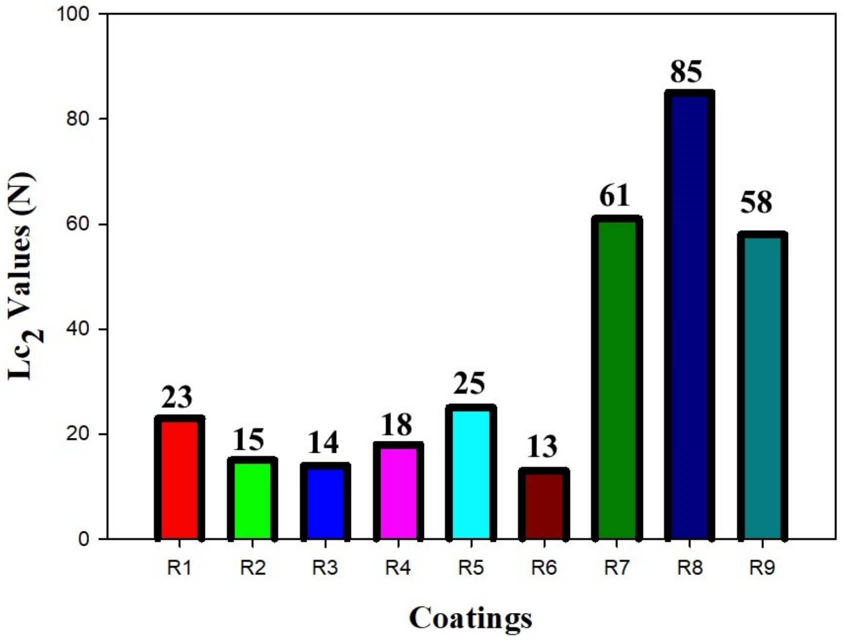


Figure 8. Lc_2 critical load of coatings

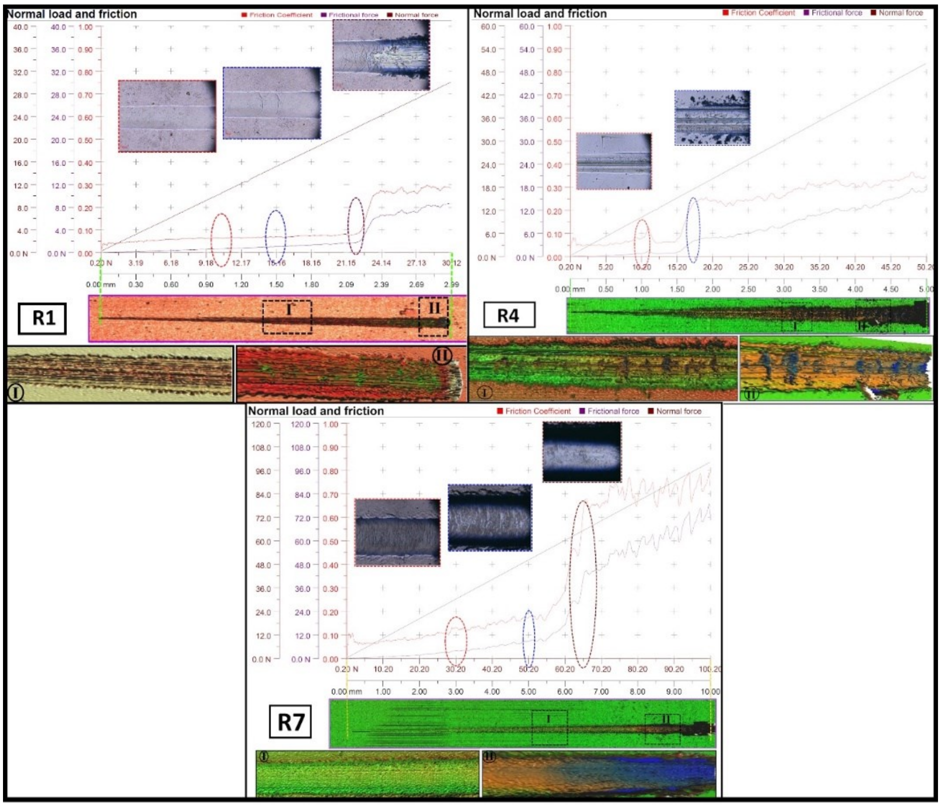


Figure 9. Scratch test results for R1, R4, and R7 coatings

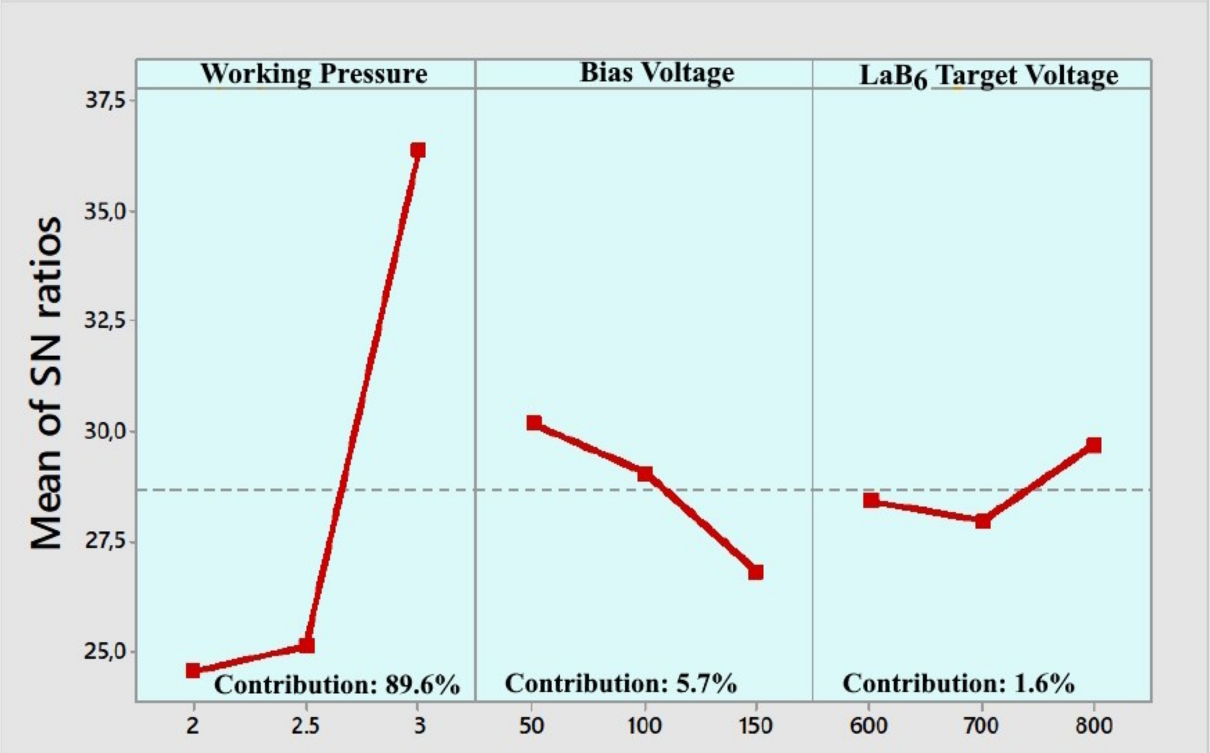


Figure 10. Average S/N Ratios for TiCrNb-hBN thin films in Lc_2 critical load

4. Conclusion

The TiCrNb-hBN thin films were deposited on DIN 1.2714 steel samples using CFUBMS system under the different deposition parameters. The microsturucture, nanohardness, adhesion strength properties of coatings were investigated. In addition, the degree of contribution of the variable parameters to these features was revealed by ANOVA analysis.

1- TiCrNb-hBN coatings, which have a novel design and recipe, are successfully produced in a granular, smooth and dense structure, free from deposition defects encountered in other coating methods.

2- The thickness of the coatings is achieved in the range of 874 nm and 1.69 µm.

3- The parameter that has the highest contribution to coating thickness values is working pressure with 63.65%.

4- All TiCrNb-hBN coatings increase the nanohardness of the DIN 1.2714 steel sample.

5- The highest hardness value is obtained in the R8 coating with a value of 24.67 GPa. This hardness achieved is approximately 400% superior than the hardness value of the substrate.

6- The highest adhesion strength is achieved in the R8 coating with a value of 85 N. There is a correlation between hardness and adhesion strength values in coatings.

7- Numerical values obtained as a result of ANOVA analysis show the degree of contribution of each parameter to the coating properties. It is a known fact that each coating parameter has different effects on the properties of the coating. This change in numerical data indicates that the effects of each of the parameters designed according to Taguchi on the coating properties are different.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

Author Contributions

Yaşar Sert: Conceptualization, Methodology, Data, curation, Writing – original draft preparation.

Tevfik Küçükömeroğlu: Supervision, reviewing and editing.

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