RESEARCH ARTICLE

Quantification of the Effects of Coating Parameters on the Properties of TiAlZrN Coatings

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Abstract

In this study, TiAlZrN layer was coated on AISI H13 substrate surface with variable substrate bias voltage, Zr target current, and ambient pressure deposition parameters by using closed field unbalanced magnetron sputtering (CFUBMS) technique. The main goal of this paper is to determine the effect percentages of these variable parameters on the properties of TiAlZrN coatings by Analysis of Variance (ANOVA). These coating properties include average grain size, thickness, hardness, adhesion strength and wear resistance. The numerical data obtained as a result of this study will shed light on the select of parameters which have a direct effect on coatings to the researchers who will work on this topic. The parameters used as variables in the deposition process were leveled with Taguchi experimental (3³) design method. Average grain size and thickness of coatings were established by SEM images. The average grain sizes of coatings were between 290 and 440 nm and the most effective parameter was substrate bias voltage with 58.4 %. The hardness, adhesion strength and wear properties of the coatings were determined using micro hardness tester, scratch test and ball on disc wear device respectively. The maximum hardness of coatings was 1674 HV, while the wear resistance was increased by 37 times compared to the substrate material. The maximum adhesion strength value of the coatings was reached 56N. The superiority of the effect of substrate bias voltage on the hardness, adhesion strength and wear resistance of the coatings compared to other deposition parameters was again prominent (respectively 86.15%, 53.63% and 70.86%). Also, the hardness and wear resistance properties were found to be directly related to each other. The sample with the highest coating hardness also showed the highest wear resistance performance. In the sample with the lowest hardness, this situation found to be similar.

Keywords: TiAlZrN, CFUBMS, Taguchi, ANOVA, adhesion strength, wear

1.Introduction

The enhancement of the hardness and wear performance of the mechanical parts used in the industry is a very popular topic these days [1-3]. As a result of the studies carried out within this scope, surface coatings have come to the fore owing to their splendid advantages (high hardness and wear performance) them provide [4,5]. Some methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD), thermal spray, sol-gel and micro-arc oxidation etc. have been used for these surface coating applications over the years [6]. PVD methods stands out among these methods and within the PVD methods, CFUBMS technique is widely used due to its high deposition rate, high adhesion, high homogeneity and usability for variety of substrate materials [7-10]. The nitride based thin hard coatings were usually produced with this method which has these wonderful advantages [11,12]. In a study by Keles et. al. it was emphasized that c-BN coatings produced with CFUBMS technique significantly increased the hardness and wear properties of 4140 steel substrate [13]. Additionally, in this study, increasing the target voltage used in the coating process improved the properties of c-BN coatings. Rupetsov et. al. investigated the properties of multilayer nitride coating produced by CFUBMS. According to this study, the service life of 1.2419 tool steel was increased approximately 3 times owing to this multilayer nitride coating [14]. As can be seen from these and many studies, the coatings deposited on the substrate surface using

CFUBMS are very successful. Nowadays, it is known that the coating properties are determined by the structural properties that occur during the deposition process. The structural properties of coatings are depending on many parameters such as target current, substrate bias voltage, substrate temperature, ion current density, the distance between target and substrate, the placement of target and substrate, ambient pressure, duty time and frequency. Since these parameters used in the deposition process constantly interact with each other, each combination of these parameters creates a unique structure. Therefore, it is practically impossible to control the coating properties by considering any of these parameters independently of the others [15,16]. In the investigation of the parameters affecting the properties of coatings, it was widely used to one parameter as a variable and keep the others constant. However, in this technique, all possible variations of many parameters to be tested to obtain the best (optimum) coating properties require long operating time and high cost. In order to avoid this negativity design of experimental (DOE) methods which provide optimization of complex process have been developed by considering many variables at the same time [17-19]. Among the experimental design methods, Taguchi is one of the most common method. In this method, the results obtained from experiments performed by changing several parameters at the same time are analyzed by converting them to Signal/Noise (S/N) ratio. Here, the signal (S) is the actual value to be measured and the noise (N) is the efficiency of the undesirable factors within the measured value. It can be observed from the S/N graphs whether any parameter is effective or not. In

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Received 14 April 2020 Revised 23 April 2020 Accepted 24 April 2020

<https://doi.org/10.36937/ben.2020.004.001>

Brilliant Engineering 4 (2020) 1-8
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addition, the degree of effect of parameters can be calculated using the delta statistics determined using S/N ratios. The delta statistics are calculated by taking away the smallest of the S/N ratio from the highest. In the Taguchi method, S/N ratios are analyzed with 3 different criteria; smaller is better, larger is better and nominal is better. In some studies, in the open literature, it has been tried to make some explanations about the effects of these deposition parameters on the coating properties [20,21]. However, the parameters effect on the coating properties have not been investigated numerically in these publications in the open literature. In the studies carried out using multiple variable parameters, it is a deficiency that these degree of effects are not determined concretely because each parameter will have its own effects on the coating. In this study, L9 (3³) orthogonal sequence was used for experimental design. The variable parameters are target current, substrate bias voltage and ambient pressure and these variable parameters were leveled at 3 different values. The data in each experiment in the orthogonal sequence were analyzed with the ratio giving the performance of the statistical measurement called S/N. Thus, it is aimed to eliminate the deficiency in the open literature.

2. Experimental Procedure

2.1. Preparation of Samples

AISI H13 (X40CrMo5-1) tool steel designated as the substrate material in the coating process was purchased commercially in the form of a cylindrical bar. These steels were subjected to machining in 30mm diameter and 4mm thickness. Cutting tool marks on the surface of machined steels were cleaned by sanding. The samples were hardened according to the literature [22]. These hardening processes include stress relief annealing at 650°C, oil cooling at 1030 °C and finally repeated tempering at 500 and 600 °C. Rough-fine sanding and polishing processes were carried out respectively to prepare as far as minimum roughness (~0.05µm) before coating process of the hardened substrates. The hardness of the samples prepared with the metallographic processes mentioned above is at the level of 550 HV_{0.025}.

2.2. Details of Coating Method

In this study, pulsed DC closed field unbalanced magnetron sputtering (CFUBMS) method was used for producing TiAlZrN thin hard coatings which are expected to positively affect the service life and usage performance of AISI H13 steels. In this method, by creating a closed magnetic field with four magnetrons, the plasma is kept within the magnetic field lines and the atoms which are sputtered from the targets (two Ti targets, one Al and Zr target) are directed to surface of the samples more intensely. The most important advantage of the system being unbalanced is providing plasma formation away from the magnets. Thus, some disadvantages such as the target poisoning and arc formation on the surface are not encountered in this process.

Table 1. Coating Parameters

Parameters	
Counter body	Al ₂ O ₃ (~15GPa)
Diameter of counter body	6 mm
Number of Cycles	1600 cycles
Test Environment	Atmosphere
Track diameter	10 mm
Peripheral Speed	60 mm/s
Constant Parameters	
Target Current; Ti / Al (A)	6 / 2
Ti Interlayer Current (A)	6
Deposition Duration (min)	60
Frequency (kHz)	100
Duty Time (μs)	2.5

2.3. Coating Process

The coating process parameters are given in Table 1. The coating process started with Ti interlayer in order to enhance the adhesion ability of the layer to the surface. As can be seen in Table 1, the current value of this Ti interlayer is 6A. Later than the Ti interlayer, TiAlZrN films were coated on the AISI H13 steel under various Zr target current, substrate bias voltage and ambient pressure. As mentioned above, these variable parameters were leveled with the Taguchi L9 (3³) experimental design using the Minitab program. (3³) stated that there are 3 levels belonging to 3 variables. The schematic of the placement of targets and magnetrons in the coating chamber is shown in Figure 1. As seen in this figure, the magnetrons were placed with opposite poles side by side to create a closed magnetic field.

Figure 1. Schematics of the CFUBMS system [23]

2.4. Structural- Hardness- Adhesion and Wear Analyses

Structural analysis and thickness measurement of coatings were carried out using scanning electron microscope (SEM- QUANTA FEG450). The average grain size of coatings was measured by using linear intercept method on SEM images. The resistance to plastic deformation of the coatings was determined by micro hardness (Struers) with Vickers indenter at 25g load in 10 seconds and scratch test (CSM brand). For scratch test, 200 µm diameter of Rockwell C type indenter was used, also experiments were carried out at 10 mm/ min speed and increased load up to 100N. Scratch tracks of coatings were characterized by SEM and ASTM standards. The wear behavior of the substrate and TiAlZrN coatings were examined using ball on disc tribometer (DUCOM). Wear tests parameters are shown in Table 2. After the experiments, the wear marks on the samples were visualized with an optical profilometer (Nanofocus) and the wear volumes were designated. The parameters affecting the findings obtained from the experiments were analyzed using the Minitab program. S / N ratios were determined for each of the parameters. Then, the effective parameters were quantified by calculating the delta statistics from these S / N values.

Table 2. Wear Tests Parameters

Variable Parameters and Levels			
Coatings	Zr Target Current (A)	Bias Voltage (-V)	Ambient Pressure (Torr)
R1	2	50	2x10 ⁻³
R2	3	50	2.5x10 ⁻³
R3	5	50	3x10 ⁻³
R4	3	75	2x10 ⁻³
R5	5	75	2.5x10 ⁻³
R6	2	75	3x10 ⁻³
R7	5	90	2x10 ⁻³
R8	2	90	2.5x10 ⁻³
R9	3	90	3x10 ⁻³

3. Results and Discussion

The coating thickness, average size of grain, hardness, adhesion strength and values of TiAlZrN coatings are shown in Table 3.

Table 3. Coating Thickness, grain size, hardness and adhesion strength of coatings

Coatings	Thickness (μm)	Grain Size (nm)	Hardness ($\text{HV}_{0.025}$)	Adhesion Strength (N)
R1	2.6	355	1405	15
R2	2.3	380	1420	40
R3	2.7	440	1456	34
R4	2.1	325	1532	42
R5	2.3	385	1540	47
R6	1.9	345	1489	45
R7	2.5	290	1674	56
R8	2.1	335	1567	54
R9	2.4	320	1596	51

Surface morphologies of the coatings obtained using SEM are given in Figure 2. The acquired average grain size using the intersection method on these SEM images are shown in Table 3. As can be seen in Figure 2, TiAlZrN coatings generally have a dense, spaceless and impeccable structures. These structures seem to be in accordance with Zone 1 defined by Movchan and Demchishin [24].

3.1. Effective Parameters Analysis on Grain Size

Figure2. SEM images of coatings surface

It has been stated that the average grain sizes were measured on these images. In this regard, S/N plots as a result of statistical analysis carried out to determine the effect of coating parameters on the average grain size are given in Figure 3. Analysis of variance for S/N ratios are given in Table 4. As can be seen in this table, bias voltage

was determined to be the most effective parameter on the average grain size (58.4%).

Figure 3. The charts of effect of coating parameters on the average grain size

As can be seen from Table 3, it has been determined that the average grain size of coatings is decreased with increasing bias voltage. The acceleration of mobility of ions which sputtered from targets was increased in plasma, and they were deposited with high energy on the substrate surface. Through, more nucleation zones were consisted of on the surface, denser and fine-grained structure were occurred [25].

Table 4. Analysis of variance for S/N ratios (Grain Size)

Variables	Sum of Squares (SQ)	Men Square (MS)	Contribution (%)
Zr Target Current	0.6805	0.3403	7.6
Bias Voltage	5.2597	2.6298	58.4
Ambient Pressure	2.3873	1.1936	26.5

When evaluated from the point of ambient pressure which the effect on the average grain size is 26,5%, The ions removed from the targets in low ambient pressure create anti backlash structure by providing them to reach the substrate with less loss of energy due to the less amount of gas atoms they can collide [26].

3.2. Effective Parameters Analysis on Thickness

The thickness of TiAlZrN coatings was measured by cross-section SEM photos of the films coated on the glass substrates. SEM photos with thickness measurements are given in Figure 4. According to the thickness measurements, the highest thickness of the coating was measured as 2.7 μm in R3 (5A Zr target current, 50V bias voltage and 2×10^{-3} Torr ambient pressure). The lowest coating thickness was determined as 1.9 μm in R6 (2A Zr target current, 75 V bias voltage and 3×10^{-3} Torr ambient pressure). S/N charts obtained as a result of statistical investigations for thickness of coating are given in Figure 5. From Figure 5, it was determined that bias voltage was the superior effective parameter and ambient pressure was the minimum effective parameter.

Figure 4. SEM photos with thickness measurements

Figure 5. The charts of effect of coating parameters on the thickness

Analysis of variance for S/N ratios is given in Table 5. According to this evaluation, while the most effective parameter on the thickness of coating was determined in bias voltage as 52.2%, the least effective parameter was ambient pressure as 6.9%.

Table 5. Analysis of variance for S/N ratios (Thickness)

Variables	SQ	MS	Contribution (%)
Zr Target Current	2.1812	1.0906	28.2
Bias Voltage	4.0335	2.0168	52.2
Ambient Pressure	0.5335	0.2668	6.9

If the thickness of coatings was evaluated from the point of bias voltage which is the most effective parameter, in the sample group (R1-R4-R7) where the ambient pressure was kept constant at 2×10^{-3} Torr, the highest thickness was observed in R1 with the lowest bias voltage. This can be explained by the fact that the atoms which are reached with a high level of kinetic energy on the substrate surface were exposed to the ion peening effect [27]. With this effect, the

coating thickness deposited on the substrate has decreased. However, when substrate bias voltage was enhanced to 90V, thickness of coatings increased slightly due to exceed the ion peening effect.

3.3. The Effective Parameters Analysis on Hardness

The values of hardness of TiAlZrN coatings are presented in Table 3. As can be seen from this table, while the superior hardness (1647 HV) was obtained from R7, the minimum hardness (1405HV) was observed from R1. S/N graphs obtained as a result of statistical investigations for hardness of coating are given in Figure 6. In this figure, it was exhibited that the most effective parameter on hardness is bias voltage as in other properties. The values obtained in the continuation of the analysis are given in Tables 6, and the percentage of bias voltage effect was determined to be 86.15%.

Figure 6. The charts of effect of coating parameters on the hardness

Table 6. Analysis of variance for S/N ratios (Hardness)

Variables	SQ	MS	Contribution (%)
Zr Target Current	0.2322	0.116	11.8
Bias Voltage	1.6806	0.840	86.15
Ambient Pressure	0.0357	0.017	1.79

In order to reveal the effect of bias voltage, in coating groups which Zr target current is 2A (R1-R6-R8). It was observed that as the bias voltage enhanced, the hardness was in increasing trend. In this group, the superior hardness was determined at R8 and the lowest at R1. This situation can be attributable to several points. The first one is the grain boundary hardening phenomenon which is the important strengthening mechanism. Since the grain boundaries prevent the dislocation movements during deformation, the finer grain structure has more resistance to plastic deformation. The average grain sizes shown in Table 3 confirm this approach. Another approach is related to the nitrogen content of coatings. In this group, the coating which has the most nitrogen content showed the minimum plastic deformation resistance. This negative effect of nitrogen content on the hardness is due to the fact that it forms an amorphous structure in the structure. This situation is associated with reduction of fine grains within this amorphous structure and thus decreasing the hardness [28]. These findings are compatible with the studies in open literature. Zhang et. al. emphasized that the hardness of coatings improved with increased bias voltage. In related study, the reason for this was attributed on the increasing compressive stress by creating preferential regions on the substrate surface with enhanced bias voltage [29]. In a similar study, it was achieved to improve the hardness by increasing bias voltage used in the production of TiZrN coatings [21]. The same results were found in other groups in which bias voltage was chosen as a variable. The bias voltage which is the most effective parameter on hardness has clearly shown its effect on the other coating groups. Also, amongst all coatings R7 was shown the highest plastic deformation resistance. It is a known fact that bias voltage and ambient pressure have opposite effects on the coating properties [30]. Since, looking at the R7 coating parameters, it was seen that the highest Zr target current and bias voltage, also minimum ambient pressure.

3.4. Effective Parameters Analysis on Adhesion Strength

Adhesion strength values of the TiAlZrN coatings are shown in Table 3. From Table 3, it was seen that the superior adhesion strength was obtained in R7 as 56N, the minimum adhesion strength was obtained in R1 as 15N. S/N graphs obtained as a result of statistical investigations for adhesion strength of coating are given in Figure 7. As can be seen from this figure, Delta statistics reached the highest value in bias voltage. The analysis of variance for S/N ratios are shown in Table 7. As a result of analyzes, bias voltage was determined as the highest effective parameter (53.63%) on the adhesion strength of the coatings.

Figure 7. The charts of effect of coating parameters on the adhesion strength

Table 7. Analysis of variance for S/N ratios (Adhesion Strength)

Variables	SQ	MS	Contribution (%)
Zr Target Current	12.9	6.451	12.58
Bias Voltage	55	27.5	53.63
Ambient Pressure	15.23	7.613	14.03

Adhesion strength values were improved with increasing bias voltage in the coating group (R1-R6-R8) which Zr target current was kept constant at 2A and bias voltage was increased as 50V-75V-100V. In the open literature, this improves in adhesion strength was attributed on the denser and compact structure of the coatings owing to increasing bias voltage [31]. Thus, the direct effect of the microstructure on the coating properties was revealed. Additionally, among these coatings, the change of hardness was compatible with increasing trend of adhesion strength. It is known that the scratch test has the logic of subjecting the material to plastic deformation. Therefore, in this coating group, it is quite reasonable that R8 which has the highest hardness value showed the superior adhesion performance. Another interesting situation is that R1 which has the highest thickness of coating showed the lowest adhesion strength. The reason for this finding has been shown in the open literature as high elastic energy stored in thick coatings [32]. Similar findings were noticed in other coating groups in which the Zr target current was kept constant at 3A-5A and bias voltage was enhanced. However, amongst all coatings the superior adhesion strength was determined at R7 which has the lowest grains size and highest hardness value.

Figure 8. Scratch tracks of TiAlZrN coatings

Scratch tracks of TiAlZrN coatings on AISI H13 steels are shown in Figure 8. These tracks were characterized in accordance with the ASTM standards. The recovery spallation mechanism was observed in the R1, R6 and R7 coatings. Recovery spallation is expressed to the coating was peeled from one or both sides of the scratch track by elastic recovery due to plastic deformation in the substrate material. However, lateral cracking was observed as dominant failure mechanism in the R2, R3, R4, R6, R8 and R9 coatings. Additionally, conformal cracking was observed in R5 and abrasive scratches occurred after the coating was removed from the surface. It was determined that, Scratch track of R7 was smoother and unpolluted than the others.

3.5. The Effective Parameters Analysis on the Wear Volume of Coatings

As a result of the wear tests, the wear volumes determined by examining the tracks on the samples using an optical profilometer are given comparatively in Figure 9. As seen in Figure 9, wear performance of all coatings was higher than the substrate material. Amongst the coatings, the superior resistance of wear was determined in R7 which has the highest hardness and adhesion strength.

Figure 9. Wear volumes of samples

S/N charts obtained as a result of statistical investigations for the resistance of wear of coatings are given in Figure 10. As can be seen in these charts, the highest difference between the maximum and minimum points was determined at the bias voltage. This finding indicates that bias voltage is the most effective parameter on the wear volume values of coatings. The analysis of variance for S/N ratios are given in Table 8. As can be seen in Table 8, bias voltage was determined as the highest effective parameter (70.86%) on the wear resistance of coatings.

In many studies, it has been emphasized that the hardness and adhesion strength significantly affect the wear performance of the coatings [33,34]. The resistance of the coatings to plastic deformation appears as a distinct phenomenon when comparing wear volumes. R7 which has been determined to have the finer grains and highest plastic deformation with the effect of bias voltage also has the superior resistance of wear. This finding is also compatible with the Archard principle which reveals the relationship between hardness and wear performance [35]. Also, under R7 coating conditions, the resistance of wear of the substrate material has been impressively increased by approximately 37 times. It has been determined that as the bias voltage increases, the wear resistance of the coatings

improves significantly. In terms of the effect of the bias voltage, R5 stands out as an exceptional coating. The reason for this can be explained from the SEM images of the wear tracks given in Figure 11.

Figure 10. The charts of effect of coating parameters on the wear volume

Table 8. Analysis of variance for S/N ratios (Adhesion Strength)

Variables	SQ	MS	Contribution (%)
Zr Target Current	13.67	6.83	4.51
Bias Voltage	214.60	107.30	70.86
Ambient Pressure	32.98	16.48	10.89

According to this figure, micro-welds were broken due to adhesive wear which is the dominant failure mechanism increased the amount of wear with the effect of third body in the coating. The predominant mechanism in all coatings was adhesive wear and abrasive scratches (third body effect) caused by it. In addition, flaking mechanism was encountered in R3 and R7 coatings. Finally, it can be seen that the wear track of the R7 which showed superior wear resistance was very smooth.

Figure 11. SEM images of wear tracks

4. Conclusions

In this study, TiAlZrN was coated on the AISI H13 steels by using CFUBMS. Zr target current, bias voltage and ambient pressure were selected as variable parameters in this coating process. As result of experiments, the degree of effects of the coating parameters on the coating properties and the inferences about these effects are given below.

- ❖ The most effective parameter to the morphological properties of the coatings was determined as bias voltage with 58.4%. As the bias voltage increased, denser and fine-grained structure was obtained.
- ❖ The parameter that has the greatest effect on the thickness of the coatings was bias voltage. The reason for the decreased thickness of coatings as bias voltage increases was attributed on the ion peening effect.
- ❖ As well as in other properties, bias voltage stands out as the most effective parameter in hardness, adhesion and wear performance.
- ❖ Linear correlation in hardness, adhesion and wear properties was revealed. In this correlation, it was emphasized that the resistance of the coatings to plastic deformation was effective.
- ❖ Adhesive wear was observed as the dominant wear mechanism in the coatings. The third body effect mechanism which was observed due to the breaking of adhesive bonds affected the wear volumes.
- ❖ The wear performance of AISI H13 steel was improved approximately 37 times owing to TiAlZrN coatings.

Acknowledgment

This study was funded by the Scientific and Technological Research Council of Turkey (TUBITAK). Grant No: 116M734. The authors would like to thank to TUBITAK for supporting this project.

Declaration of Conflict of Interest

The authors declare that there is no conflict of interest.

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