STUDY THE INFLUENCE OF TECHNOLOGICAL PARAMETERS ON THE ADHESION OF THE CrN HARD COATING TO THE SKD11 STEEL SUBSTRATE WAS MADE BY DC PULSE MAGNETRON SPUTTERING METHOD

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ABSTRACT

The hard coating CrN (chromium nitride) is a type of surface coating widely used in the manufacturing industry, automotive industry, oil and gas industry, aerospace applications, and other industrial applications. The adhesion strength of the CrN hard coating to the SKD11 steel substrate is an important property determining the applicability of the coating and is determined by the method and technological parameters during the coating process. The content of this study investigates the influence of gas flow rate, pulse frequency, substrate temperature on the adhesion strength of the CrN hard coating to the SKD11 steel substrate created by the pulsed DC sputtering method.

Keywords: *SDK11 steel, Hard coating, CrN, Adhesion.*

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1. INTRODUCTION

In the world, hard coatings (with thickness measured in nanometers or micrometers) protect the surfaces of mechanical machining tools such as cutting tools, shaping tools, various types of pressure die casting molds, etc., in order to reduce wear and scratches, enhance the durability and lifespan of the tools [10-12]. Leading countries in science and technology like the United States, Japan, Germany, and South Korea have been, are currently, and continue to invest in researching and manufacturing various types of hard coatings and materials with exceptional properties for special applications in aerospace and defense industries. Additionally, countries in the region such as Taiwan, China, and Thailand are also heavily investing in surface technology, including the production of protective hard coatings, and have achieved commendable achievements. For example, companies like Fujilloy Co., Ltd. in Thailand and Zhejiang Huijin in China have successfully manufactured and commercialized some types of hard coatings.

PVD is a general term used to refer to the technology of creating hard film layers by depositing materials in vapor phase onto the surface of a sample or component in a vacuum environment through physical processes. PVD technology has been in use for over 30 years and is increasingly applied widely to produce protective hard film layers on the surfaces of components and tools [13-14]. The PVD process consists of three main stages: Material evaporation or extraction from the source; Transportation: moving the material to the surface to be coated; Deposition: creating a film layer on the surface of the target sample.

Among the various types of hard coatings currently under research and widespread use [15-18], CrN films possess several characteristics. These include high hardness (approximately 1800 - 2100HV), low friction coefficient, excellent heat resistance (stable up to 700°C), good resistance to wear and abrasion [1-6]. Furthermore, CrN is an inert material (does not react with most chemicals) and stable, with strong adhesion capabilities, forming molecular bonds with the substrate material. It can be applied to a wide range of different substrate materials. Additionally, CrN is non-toxic, making it suitable for coating tools used in surgery or food processing equipment. Thanks to these advantages, CrN hard coatings have the potential for widespread applications in the manufacture of automotive engine components, cutting tools, certain types of pressure die-casting molds, or metal stamping dies.

The adhesion of CrN hard films to the substrate is an essential characteristic that determines the applicability of the hard film and depends on the method as well as the technological parameters during the film formation process [19-22]. Many research studies have investigated the properties of CrN hard films fabricated using the PVD (Physical Vapor Deposition) technique. Among these, the pulsed DC sputtering method is a PVD technique for depositing compound coatings in a plasma environment. It offers advantages such as not requiring extremely high vacuum conditions, controllable processing, absence of arc discharges, the mitigation of target poisoning, low process temperatures, high ion energy in the plasma, and high deposition efficiency, making it suitable for creating CrN hard coatings on SKD11 steel samples.

According to research results [23-27], it has been shown that SDK11 steel is suitable for use in cold forging dies. When both I and the SKD11 steel achieve a hardness of approximately 58-60 HRC, the strength and toughness are in line with the requirements of the material for cold forging dies. With these properties, cold forging dies made from SKD11 material mainly improve the phenomena of fatigue, cracking, and elastic deformation during the working process of the dies.

In this study, the research team manufactured samples from SKD11 steel and coated them with CrN hard films using the pulsed DC sputtering method. Subsequently, they conducted an investigation to determine how various technological parameters during the coating process affect the adhesion of the CrN hard film to the SKD11 steel substrate.

2. THEORETICAL FOUNDATION/RESEARCH METHODOLOGY

2.1. The mechanism of Pulsed DC Sputtering

By applying a pulsed DC voltage with a sufficiently high repetition frequency (ranging from 0 to 350 kHz) between the cathode and anode (as shown in Fig. 1), high-energy Ar+ ions in the plasma environment are used to bombard the surface of the Cr layer, effectively "removing" material from the Cr layer. The Cr atoms, after being detached from the Cr layer and colliding with other ions in the plasma environment, transform into Cr ions that move towards the substrate (SKD11 steel). During the transport process, they combine with nitrogen ions present in the environment and deposit onto the SKD11 steel substrate, forming a CrN coating layer.

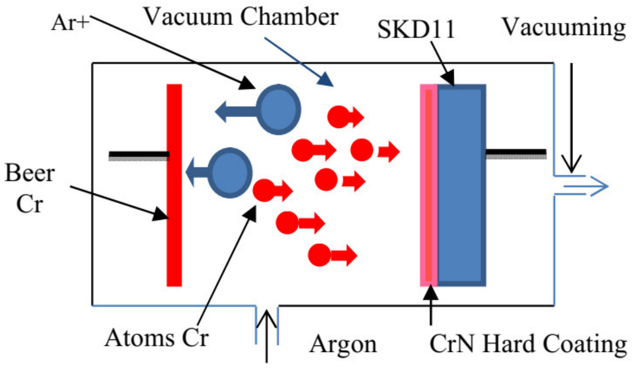

Fig. 1. DC Pulse Width Modulation Mechanism

2.2. The SKD11 steel sample serves experimental research purposes

Samples used for research must meet requirements regarding surface smoothness, surface hardness, and dimensions suitable for experimental equipment and analytical evaluation. The coated sample is made of SKD11 steel with the following chemical composition: C 1.4%, Si 0.275%, Mn 0.39%, Cr 11.24%, Mo 0.83%, V 0.205%, P < 0.017%, S < 0.0005%, with dimensions: Φ15xL5mm (Fig. 2). It is heat-treated to achieve a hardness in the range of (58÷60) HRC, and then ground and polished to achieve a surface smoothness of $R_a < 0.02\mu m$.

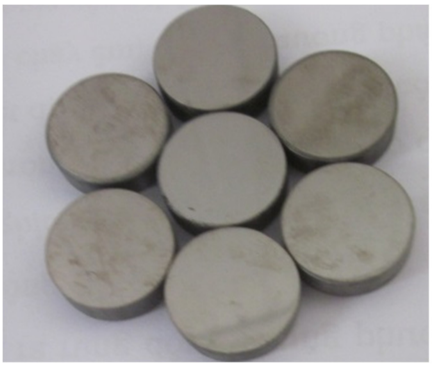

Fig. 2. Experimental Sample

2.3. Creating a CrN Coating on the Steel Sample

The deposition of the hard CrN coating using the pulsed cathodic arc method is carried out in a vacuum chamber with dimensions of 300 x 600mm. The vacuum system includes both mechanical and diffusion pumps. A magnetron sputtering head is equipped with a chromium target (99.99%) measuring 100 x 10mm. The process gases used consist of two types: Ar 99.99% and N_2 99.99%. The gas flow into the vacuum chamber is controlled by two Mass Flow Control 2179A devices from MKS. The pulsed power supply used is the Pinnacle TM plus device with a frequency ranging from 0 - 350kHz and a power output of 5kW, manufactured by Advance Energy, Inc - USA.

The fixed process parameters for creating the hard CrN coating are as follows: the distance between the substrate and target is 100mm, the Ar gas flow rate is 12 cm^3/minute, the base pressure is $8x10^{-2}$Pa, the arc current density is 1A, and the coating deposition time is 90 minutes. Three process parameters are varied to study their effects on the wear characteristics of the hard CrN coating during the deposition, as listed in Table 1 [28].

Table 1. Coating Parameters

No	Parameters	The range of values for the research parameters
1	Pulse Frequency, kHz	50 ÷ 150
2	Nitrogen Gas Flow Rate, cm^3/minute	4 ÷ 8
3	Coating Sample Temperature, °C	100 ÷ 300

Before creating the coating, the steel sample undergoes a rigorous chemical surface cleaning process to ensure that the resulting coating adheres well to the surface [7].

2.4. Method for Coating Thickness Evaluation

To determine the adhesion strength of the coating to the substrate, the scratch method is employed [9]. The measurement principle of this method is described as follows:

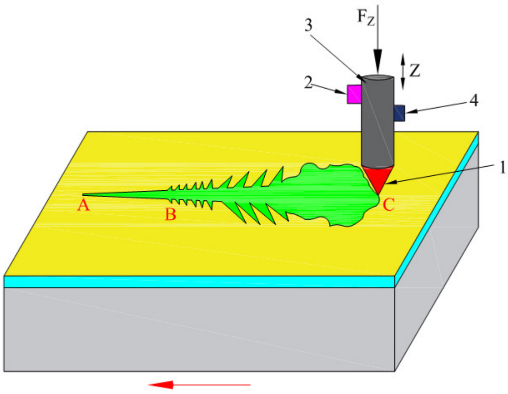

Fig. 3. Principle of Adhesion Measurement between Coating and Substrate

1 - Indentation Tip; 2 - Sound Sensor; 3 - Indentation Force Mechanism; 4 - Position Sensor

Fig. 4. UTM-2 Friction Measurement Device

In this measurement method (Fig. 3), a flat sample is placed below, and a cutting tool (1) with a radius r_0 is positioned above. On the cutting tool assembly (3), there are position sensors (4) (controlling the vertical movement of the cutting tool) and sound sensors (2) (recording the sound emitted during the cutting process). The applied load F_z on the cutting tool is controlled by a force sensor in the vertical direction.

The measurement process is as follows: initially, the cutting tool makes contact with the sample at point A, and the applied load F_z on the cutting tool is P_1 (N). Then, the cutting tool moves horizontally relative to the coated sample to point C. The distance that the cutting tool travels during the cutting process on the coated sample is L = AC (mm). While the cutting tool is moving along segment AC, two simultaneous events occur:

The applied load on the cutting tool increases linearly, and when it reaches point C, the applied load F_z on the cutting tool reaches P_2 (N). Therefore, the rate of acceleration is calculated as follows: $(P_2 - P_1)/L$ (N/mm);

As the cutting tool moves relative to the sample in the vertical direction, penetrating deeper into the sample, when the cutting tool reaches point C on the sample's surface, it simultaneously advances further into the sample by a distance of L_1 (mm). Thus, when observing the cut on the sample, it becomes apparent that the cut widens and deepens progressively from point A to C.

So, when the cutting tool moves relative to the sample along segment AC, it creates a cut into the sample, removing both the coating material and the substrate material. The adhesion strength of the coating to the substrate is evaluated using the adhesive force limit LC (N). The value of LC is determined at the position of point B along the cut, where the delamination of the coating begins. In other words, when the edge of the cut starts to exhibit a sawtooth pattern, at that point in time, the value of the force FZ applied to the cutting tool reaches LC (N) [21]. To accurately determine the position of point B on the cut, based on the sound signals recorded during the cutting tool's motion into the coated sample, as detected by the sound sensor attached to the cutting tool, at point B, there is a sudden and significant change in sound intensity, and it becomes unstable. Thus, relying on the time-based sound signals (along the cutting path) obtained from the sound sensor attached to the cutting tool allows for the precise determination of the value of the adhesive force limit LC between the coating layer and the substrate.

In the adhesion test of the CrN coating to the SKD11 steel substrate, measurements were conducted using the Universal Micro Materials Tester UMT-2, manufactured by the American company CETR (Fig. 4). This device has a maximum load (FZ) that can be applied to the sample of 200N and a maximum frequency of the sample stage of 20Hz. The testing conditions for measuring the wear rate of the hard CrN coating are as follows: a cutting tool with a radius of 200µm is used, the maximum load applied to the cutting tool is 18N, the measurement time is 30 seconds, the length of the cut is 5mm, and the rate of acceleration is 0.6 (N/s). Each experiment is performed at least three times to ensure the repeatability of the experimental results.

3. RESULTS AND DISCUSSION

To investigate the influence of three technological parameters: pulse frequency (A), nitrogen gas flow rate (B), and substrate temperature (C) on the adhesion of the CrN hard coating to the SKD11 steel substrate, a total of 15 experiments were designed using the Box-Behnken experimental design [29]. The results of measuring the adhesion of the CrN hard coating to the SKD11 steel substrate are summarized in Table 2.

Table 2. Results of measuring the adhesion strength limit of the CrN coating to the SKD11 steel substrate

No	Pulse frequency - A (kHz)	Gas flow rate - B (cm^3/minute)	Substrate temperature - C (°C)	L_C [N]
1	100	8	300	12.0
2	100	4	100	9.6
3	50	4	200	9.0
4	100	4	300	11.7
5	150	8	200	10.5
6	50	8	200	9.2
7	100	8	100	10.5

8	150	6	300	12.2
9	100	6	200	13.3
10	150	6	100	11.5
11	50	6	100	9.9
12	50	6	300	12.2
13	150	4	200	9.0
14	100	6	200	13.1
15	100	6	200	12.9

Running a data analysis program in Minitab yielded the results of a regression analysis describing the influence of three technological parameters (pulse frequency, nitrogen gas flow rate, and substrate temperature) on the adhesion strength of the CrN hard coating to the SKD11 steel substrate as follows:

$$
\begin{aligned}
L_C = & -16{,}795 + 0{,}136A + 6{,}385B + 0{,}021C \\
& - 6{,}288.10^{-4}A^2 - 0{,}532B^2 - 9{,}722.10^{-6}C^2 \\
& + 0{,}002A*B - 8{,}1.10^{-5}A*C
\end{aligned}
$$

The determination coefficient (R-Sq = 98.56%) and the adjusted determination coefficient (R-Sq(adj) = 95.16%) indicate that the regression model fits the measured data very well.

The response surface model illustrating the interaction of the three technological parameters, pulse frequency, nitrogen gas flow rate, and substrate temperature, on the adhesion strength of the CrN coating to the SKD11 steel substrate is presented in Figs. 5, 6, and 7.

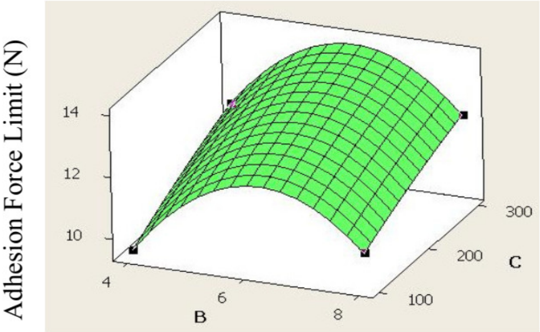

Figure 5. Graph Showing the Adhesion Strength of CrN Coating to SKD11 Steel Substrate as a Function of Nitrogen Gas Flow Rate and Temperature at a Frequency of 100kHz

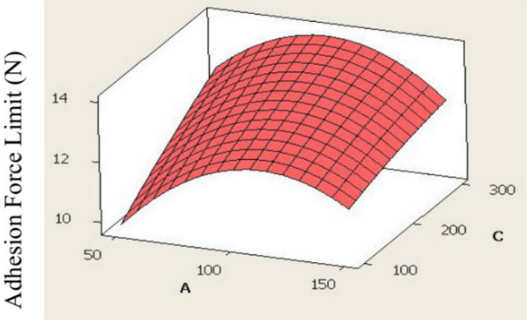

Fig. 6. Graph Showing the Adhesion Strength of CrN Coating to SKD11 Steel Substrate as a Function of Pulse Frequency and Temperature at a Nitrogen Gas Flow Rate of 6 sccm

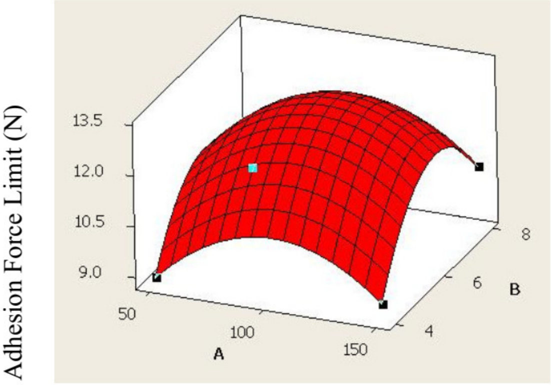

Fig. 7. Graph Showing the Adhesion Strength of CrN Coating to SKD11 Steel Substrate as a Function of Pulse Frequency and Nitrogen Gas Flow Rate at a Temperature of 200°C

From the experimental regression analysis combined with the graphs depicting the dependence of adhesion strength of the CrN coating to the SKD11 steel substrate on pulse frequency, nitrogen gas flow rate, and substrate temperature (Figs. 5, 6, and 7), the following observations can be made:

The most significant impact on the adhesion strength of the CrN coating to the SKD11 steel substrate, when deposited using the DC sputtering method, is the nitrogen gas flow rate, followed by pulse frequency, while substrate temperature has the least influence.

Second-order and interaction effects of these parameters on the adhesion strength of the CrN coating to the SKD11 steel substrate are also clearly evident. However, the interaction parameter BxC shows no significant impact on adhesion strength.

Parameters with a positive sign (+) indicate a direct influence, increasing the adhesion strength of the CrN coating to the SKD11 steel substrate. Conversely, parameters with a negative sign (-) have an inverse influence, reducing the adhesion strength.

The strongest influence of nitrogen gas flow rate on the adhesion strength of the CrN coating to the SKD11 steel substrate is observed within the research range of 4 to 8 sccm (nitrogen gas flow rate). This range is the primary cause of variations in adhesion strength, and the optimal nitrogen gas flow rate for adhesion strength lies within this research range.

The effect of pulse frequency on the adhesion strength of the CrN coating to the SKD11 steel substrate is significant within the research range of 50 to 150kHz. This range contributes to variations in adhesion strength, and the optimal pulse frequency for adhesion strength is within this research range.

Substrate temperature has the least impact and exhibits a linear relationship with the adhesion strength of the CrN coating to the SKD11 steel substrate. Within the research range of 100 to 300°C, the highest adhesion strength is achieved at a substrate temperature of 300°C.

4. CONCLUSION

In this article, the group of authors conducted a study on the creation of a hard CrN coating on the SKD11 steel substrate using the pulsed DC sputtering method. Subsequently, they proceeded to investigate the impact of pulse frequency, nitrogen gas flow rate, and substrate temperature during the coating process on the adhesion strength of the CrN coating to the SKD11 steel substrate. The results showed that varying the values of these process parameters, namely pulse frequency, nitrogen gas flow rate, and substrate temperature, led to changes in the energy of ions within the plasma of the coating chamber, resulting in alterations in the properties of the fabricated hard coating layer. The most significant influence on the adhesion strength of the CrN coating to the SKD11 steel substrate deposited using the pulsed DC sputtering method was the nitrogen gas flow rate, followed by pulse frequency, with the least impact being attributed to the substrate temperature.

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