PREAMBLE

1. Reason for choosing the topic

In the world, the hard coating is used to protect the instrument surface of the mechanical machining process such as cutting tools, forming tools, pressure processing molds ... to reduce abrasion and scratches, increased durability and lifespan of instruments. The leading countries in science and technology as the US, Japan, Germany, and South Korea have invested in research on manufacturing the hard coating and materials with transcendental features used in special applications in space industry and defense. Besides the countries in the region such as Taiwan, China and Thailand have also had strong investment for surface technology including fabrication of hard coating for surface protection and obtained the encouraging achievements.

In recent years, the hard coatings have began to receive more attention from domestic scientists and engineers. Through e state-level projects, the hard coating fabrication technology has been entered into experimental research programs on the metal cutting tools and plastic molds. These researches have mostly focused on creating hard coating on the basis of Ti material. The results obtained from the above topics at the laboratory level, have not yet been applied for commercial products. With the Cr originated-hard coatings have not yet been studied, but the adhesion of the coating to the substrate. The friction properties of the coatings are the most decisive mechanical properties to the quality and applicability of the coatings which have not been adequately assessed. On that basis, the study topic of the dissertation named **"Studying the fabrication technology of the chromium nitride (CrN) hard coating for prolonged lifespan of cold mold"** has brought scientific and technological significance and economic benefits.

2. Objectives of the study

- Selecting technological parameters of the coating process that have the greatest impact on the adhesion of the CrN coating to the steel substrate SKD11;
- Identifying the relationship between the adhesion force of the CrN coating to the steel substrate SKD11 and some technological parameters of the coating process. On that basis, the appropriate technological parameters for coating CrN on the steel substrate SKD11 are determined;
- Evaluating the friction characteristics of the CrN coating ;
- Applying to actual production.

3. Object and limitationsof the study

3.1. Study object

Study object is the process of the fabrication process of CrN coating on steel samples SKD11 with the pulsed DC sputtering method. Technological parameters are specific research objects of the topic. The adhesion of the CrN coating to the steel substrate SKD11. Friction coefficient, corrosion rate of the CrN coating and lifespan of cold molds doe coating CrN are the main parameters to evaluate the results of the study.

3.2. Limitation of the study

- Only researching the effects of technological parameters (pulse frequency, nitrogen gas flow and temperature) of the pulsed DC sputtering method to the adhesion of the CrN coating to the steel substrate SKD11 in laboratory conditions;

- Empirically determining the coefficient of friction and corrision rate of the CrN coating in laboratory conditions;

- Depositing the CrN coating on the surface of cold mold with steel molding materials SKD11, surveying lifespan of cold mold in production conditions.

4. Scientific and practical significance of the study

4.1. Scientific significance

Research results have scientific meaning including:

- Using the pulsed DC sputtering method to improve the quality of the surface of the instrument;

- Determining the impact of technological parameters (pulse frequency, nitrogen gas flow and temperature) of the pulsed DC sputtering mehtod to the adhesion of the coating to the substrate;

- Assessing the friction properties and corrosion of the coating .

4.2. Practical significance

The research results have practical significance including:

- Establishing three technological parameters: frequency pulses, the nitrogen gas flow, temperature for application for cool mold;

- Continuning to research and application of coatings created by the pulsed DC sputtering method in practice for some items and instruments.

5. Research Methodology: theory combined with experiment.

5.1. Theoretical research

- Research and the hard coating technology created on surface of instruments and items. The properties of the hard coating are made by CVD and PVD technologies. Solutions for increased lifespan of cold mold;

- Researching on the theoretical basis of the sputtering process, the pulsed DC sputtering method and the evaluation of coating properties. The method studies influences of some technological parameters of the pulsed DC sputtering process to the adhesion of the CrN coatings to steel substrate SKD11.

5.2. Experimental method:

Coating CrN on steel samples SKD11 by the pulsed DC sputtering method, then measuring the adhesion of the CrN coating to the steel substrate SKD11 in laboratory conditions, processing data measured by the experiment planning method to determine the reasonable coating parameters, identifying the friction properties of the coating. Then covering the cold mold (steel SKD11) and longevity of mold in production conditions.

6. Thesis structure

The thesis consists of 4 chapters in addition to premable and conclusion

Chapter 1: Overview of study issues

Chapter 2: Pulse DC sputtering method

Chapter 3: Materials, equipments and methods of the study

Chapter 4: Identifying the influence of some technological parameters to the adhesion of the coating to the steel substrate SKD11, evaluating the friction features of the coating and application on cold mold

CHAPTER 1: OVERVIEW OF STUDY ISSUES

1.1. The hard coating technology on the surface of items and instruments

1.1.1. Nitriding technology

Nitriding method is to diffuse nitrogen into the surface of items for the purpose of increased hardness and increased corrision resistance. Nitriding is often done at a low temperature (480 ÷ 650^{0}C) so as not to damage the structure after burning. Nitriding process consists of the following stages: analysis phase is the process of separating nitrogen atom; absorbing phase is the process that reactive nitrogen atoms are absorbed on the surface of items thanks to gravity; diffusion phase is the process that reactive nitrogen atoms absorbed on the surface of items will diffuse into the depth from the surface in conditions of relatively high temperatures (500 ÷ 650^{0}C).

1.1.1.1. Gaseous nitriding

For Gaseous nitriding, it must have the gas providing atomic nitrogen, the NH3 is one of the gases that can provide nitrogen atoms. Thus the atomic nitrogen separated from NH_3, will diffuse into the surface of items that make nitriding layer.

1.1.1.2. Nitriding in molten salt

Nitriding method in molten salt is diffused nitrogen, sulfur and carbon in the mixture tank of xianat, carbonate and sulfide; The main components of salt consits of CNO (32-38%) and carbon (17-21%). Upon nitriding, molten salt through a chemical reaction will provide (N, S, C, V) simultaneously limit cyanide concentrations increase.

1.1.1.3. Gasous carbon nitriding (C-N) at high temperature

Gasous carbon nitriding (C-N) is to put petroleum $(C_2H_4OH)_3N$ and NH_3 in to absorbent gas mixture furnace at temperature 800 ÷ 900^{0}C, the reaction produces carbon and atomic nitrogen.

1.1.1.4. Nitriding by ionization

Setting voltage from 300 to 800 V, pressure from 133.3 to 1333 Pa, specific capacity from 0.7 to 1 W/cm2. Surface of items is destroyed by gasous positive ions and heated to temperature range (450÷550 ^{0}C). Nitrogen ions are attracted to the surface of items and diffused deeply into the items.

1.1.2. Thermal sputtering technology

Thermal sputtering technology is to essentially put solid particles into the high-energy materials such as fire or plasma gas flow to accelerate solid particles, particle melting furnaces, molten bead pushed to the surface of items need to be coated.

1.1.2.1. Oxygen - acetylene sputtering method

Coating material (in form of wires or powder) is heated by the gas flame Liquid metal is dispersed into dust by compressed air and pushed at high speeds towards base metal surface that was prepared. At the surface of items, the linking process between the elements of the two-metal phases is occured to form the coating.

1.1.2.2. Sputtering method by detonating gas

This method uses a heat source generated by detonating gas with the capacity of millions of watts, speed of coating elements of 800÷1,500 m/s, temperature of 3000÷4000 °K leading to coating materials to be melt, gas to be escaped from the explosion chamber to entrained powder, led down the sputting barrel to the surface of items.

1.1.2.3. Sputtering method by electric arc

The essence of the electric arc method is to takr advantage of electric arc flame to heat coating materials, then use pressure gas line to blow the liquid metal drops into a high velocity stream of dust towards the surface of basic items.

1.1.2.4. Plasma sputtering method

Plasma sputtering nozzle consists of cathode and anode in tubular form. Arc is formed when closing the circuit between the cathode and anode. Nitrogen or argon gas stream is simultaneously fed into the sputtering nozzle. Plasma flame is formed when gas stream meets arc. Material is fed into the high temperature zone and is heated, then blown into dust and fied at high speeds towards the basic surface.

1.1.3. CVD technology

CVD technology is to create a coating by chemical deposition from the vapor phase. CVD process is performed by introducing the singlechemical substance (or compound) in vapor into a reaction chamber containing the items need to be coated. In the chamber, the chemical reaction occurs on or adjacent surface of items need to be coated and reaction products will deposit (hard coating material layer) to the surface of items. Chemical reaction will occur at temperatures required for the reaction occurrence (typically 700÷1000 °C). CVD methods often use TACVD CVD, PECVD, PACVD ...

1.1.4. PVD technology

PVD Technology is to coat by physical deposition from the vapor mixture. This process is done according to the following stages:

- Converting materials need to be deposited from the solid phase to a vapor phase;
- Transporting materials from evaporation source through low gas pressure environment in the chamber to the surface to be coated;
- Depositing vapor of coating materials needed to form the coating.

1.1.4. 1. Evaporation method in vacuum

Heat is provided from resistors, current sensors or electronic beam.

1.1.4.2. Sputtering method

When the solid surface may be destroyed by the high-energy ion, the atoms can be moved away from the surface. In this process the solid substance play role as sputtering stele, energy particle beam (ion or molecule) or positive ions produced in plasma, are accelerated to the negative bias voltage stele.

1.1.4.3. Vacuum arc method

Based on the principle of creating a plasma with a high temperature, cathode polarization > 1kV, large plasma density is used to create metal coatings, alloys, compounds through chemical reactions with plasma and materials of items. The coating of items with large size is created by the collaboration with the electron gun. The coating with large thickness and highly-packed levels, the adhesion of the coating to the substrate is good.

1.1.4.4. Ion implantation method

Ion implantation method uses high voltage (> 100 kV) or extremely high voltage pulse. Ion implantation method is to create a perfect hard coating in both structure and quality as well as create a coating rate. However,due to the current high cost, this technology is mainly used for the aircraft industry and space technology.

1.2. Features of the hard coating

1.2.1. The hardness of the coating

The hardness of the coating is an decisively important feature to abrasion resistance of the coating. The hardness of the coating depends on the microstructure of the coating as phase, the particle size ...

1.2.2. Adhesion of the coating to the substrate

Adhesion of the coating to the substrate is the most important feature deciding the lifespan and performance of the coating items. The adhesion of the coating to the substrate depends primarily on creating methods of the coating and and teh surface before coating.

1.2.3. Friction features of the coating

Friction coefficient of the coating is one of the important characteristics to determine abrasion resistance, adhesion resistance of the coating. The friction coefficient of the coating depends on the creating method of the coating and coating materials.

1.2.4. Corrosion features of the coating

Corrosion resistant of the coating is one of the important features deciding the applicability of the coating. The corrosion of the coating depends on the friction coefficient of the coating, the ability of the membrane adhesion to the substrate, the microstructure of the coating.

1.3. Application of CrN hard coating on a cold mold

1.3.1. CrN hard coating

CrN hard coating is resistant to corrosion and high abrasion, relatively small friction coefficient and hardness, the adhesion of the coating to the high substrate. The method used to create CrN hard coating is the sputtering method and the vacuum arc method.

1.3.2. Application of CrN hard coating on a cold mold

In the process of shaping by cold mold, billetslide relatively on the surface of the cold mold under high pressure contact, thus the following symptoms are appeared on cold mold including: abrasive adhesion, abrasion, fatigue corrosion, cracks and the phenomenon of plastic deformation. With steel SKD11 as material of mold, it mainly improves fatigue, cracks and plastic deformation in the working process of mold. For abrasive adhesion reduction, abrasion on the surface of cold work mold must reduce friction, increase hardness of working surface of cold mold. Therefore one of the solutions to solve the problem that is to create the hard coating on the working surface of cold mold. In the coatings for reducing friction, increasing wear resistance, CrN is one of the material anticipated as chemical durability and resistance to chemical corrosion and scratches, low friction coefficient appropriate to cover up cold surface of the mold. In the sputtering mehod, the pulsed DC sputtering method - one of compound coating generated by physically coating in plasma environment (PVD) does not required the high vacuum, can control the working process, does not appear the phenomenon of arcing, overcome toxicity of stele, the low temperature in the coating process, high ion energy in the plasma, high performance of deposition to form a hard coating on the working surface of cold mold with a substrate material as steel SKD11.

Conclusion of Chapter 1

- The hard coatings with a thickness of several nanometers to several tens of μm fabricated by PVD technology does not alter the structure of the substrate as well as the geometric shape of the surface coated. However, they are highly resistant to abrasion and chemical attack with low friction coefficient and high hardness, thus very suitable for use to protect softer surfaces without the fabrication of mass materials, bringing about high economic efficiency especially with the rare and expensive materials.
- In order to reduce friction, abrasion, especially sticky corrosion on the working surface of the cold dies with the purpose of improving the life of cold dies, it is required to create the hard coatings to the working surface of cold dies. CrN hard coating is expected to be the material with suitable properties to cover the working surface of the cool dies.
- The pulsed DC sputtering method of PVD coating technology is sputtering method using pulsed DC voltage source that can control the working process and shall not appear the phenomenon of arcing,low temperature in the coating process, high ion energy in plasma and high sputtering performance that is an effective method to create the CrN hard coating on the working surface of cold mold (mold material as steel SKD11) to increase the lifespan of the cold mold.

CHAPTER 2: THE PULSED DC SPUTTERING METHOD

2.1. Theoretical basis of creating the coating by the sputtering method

2.1.1. Sputtering mechanism

Stele made from metal material M is splashed by the high-energy ion and sputtered and aggregated on items. In the process of ion- solid interaction, the energy transmitted to the atom M and these atoms are sputtered from the stele surface.

2.1.2. Sputtering performance

Sputtering performance Y is the ratio of atom of stele material splashed out of stele and number of ions to the stele surface.

2.1.3. Factors affecting to sputtering performance

Sputtering performance Y depends on the mass of ions and ion energy. These factors are primarily determined by the relationship between the voltage between the electrodes and the sputtering pressure.

2.2. The theoretical basis of magnetic sputtering

2.2.1. The motion of electrons in parallel electric and magnetic fields

In a magnetic filed, electronic time present in the plasma will last longer and so will increase the likelihood of collision of ions, the electric discharge line will grow stronger and increase the sputtering rate. Compared to the simple DC sputtering configuration, this configuration operates in the line and at greater air pressure. Therefore, when a magnetic field, increased capability of splasted electronics on surface of items and the working ability in the same vacuum level also increased.

2.2.2. The motion of electrons in perpendicular electric and magnetic fields

When using a magnetic field parallel to the stele surface and perpendicular to the electric field,y the electrons initiall emitted from the cathode to the anode perform a spiral motion in the movement process, but when the electrons contact parallel magnetic field, their orbits are bent back on stele. By orienting magnets and stele appropriately, "the running" can specify where the electrons jump circle at high speed causing abrision of stele, due to when working, ionization occurs most powerful within this circle.

2.3. The pulsed DC sputtering method

2.3.1. Operational principle of the pulsed DC sputtering system

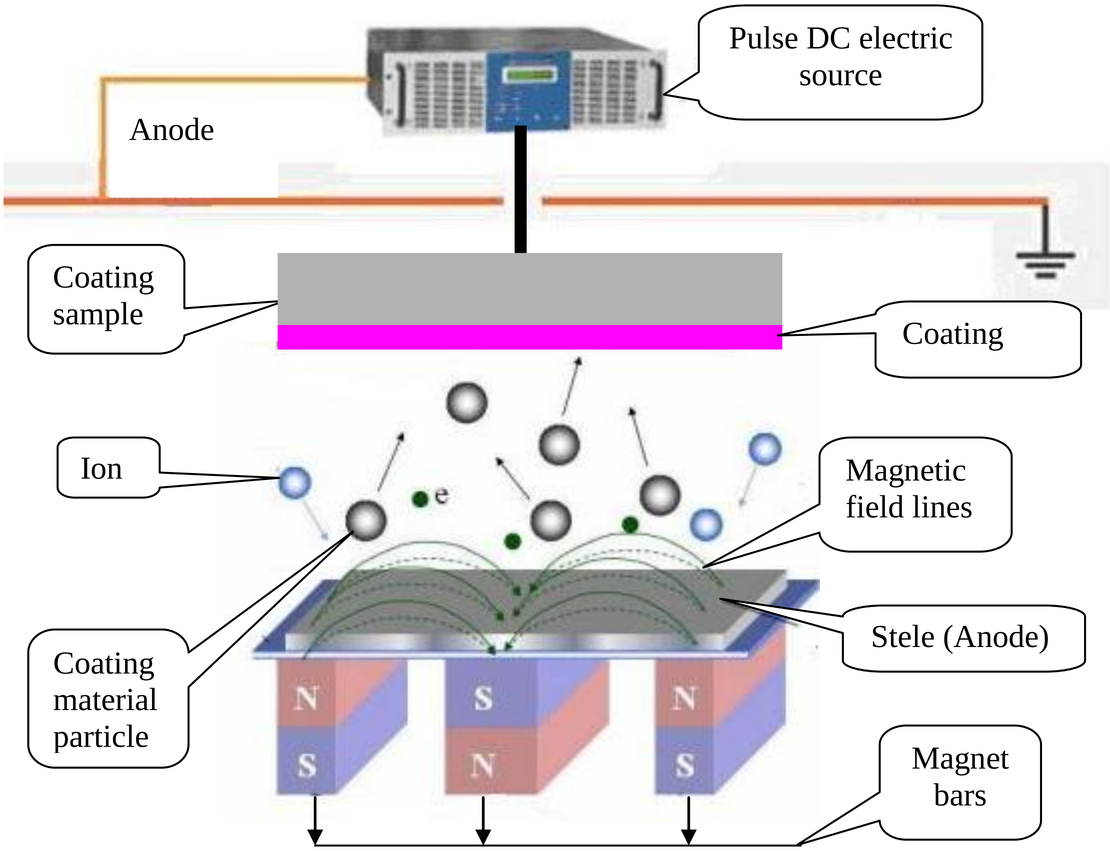

Figure 2.1. Operation principle of of the pulsed DC sputtering system

According to the diagram Figure 2.1, the sputtering nozzle includes magnet system to form magnetic clusters so that the magnetic vector B is parallel with the cathode surface. The pulsed DC voltage source is connected with the cathode and anode to generate electric field with electric field strength vector E perpendicular to the cathode surface. Such vectors E and B are perpendicular to each other. When moving in the electromagnetic field, charged particles will be affected by the Lorentz force, the greater the intensity electric field generated between two electrodes with the appropriate pressure, plasma also known as gas discharge phenomena in the poor are shall be appreared in the space between two electrodes. The positive ions generated in the discharge will be accelerated by the electric field on spashed into the cathode. If the energy of ions is big enough and its dynamics passes to the greater material atoms than a limit, also known as the free energy (specific for each material) will have atomic or molecular material escaping from the cathode surface and this atom being deposited on the surface of the sample.

2.3.2. The influence of some technological parameters of the coating process by the pulsed DC sputtering method

2.3.2.1. The influence of content (flow) of nitrogen

When content (flow) of nitrogen changes, it shall change the structure, chemical composition, organization and coating deposition rate.

2.3.2.2. The influence of pulse frequency

When the pulse frequency changes, it shall change the roughness, hardness, adhesion force of the coating to the substrate and coating deposition rate.

2.3.2.3. The influence of temperature of coating sample

When temperature of coating sample changes in the coating process, it shall change the roughness, hardness, adhesion force of the coating to the substrate, the coating deposition rate and especially the diffusion of the coating.

2.4. Studying and cleaning the sample surfaces before coating

Surface treatment before coating is a very important part of the coating process, it decides more on the quality of the coating and especially the adhesion of the coating to the substrate. So surface treatment is the key.

2.4.1. Cleaning the surface by chemical method

Cleaning by chemical method for the purpose of removing grease and solid contaminants is done primarily on the surface of items, including hydrophobic and non-hydrophobic area.

2.4.2. Cleaning in coating chamber

Cleaning the chamber aims to clean up government layers on dirties coated surface that chemical cleaning methods are not disinfected.

Conclusion of Chapter 2

- The coating is formed by high ion energy splashed on the stele surface made out of atoms on the stele surface, these atoms move in the plasma environment and deposit on surface of items to form the coating.

- Sputtering performance depends on ion line splashed on the stele surface. The energy of this ion flow depends on the relationship between the voltage (current) between the electrodes and the pressure in the sputtering chamber.

- In magnetic sputtering, upon electric field (E) and magnetic field are perpendicular each other on the surface of the stele, this effect increases the sputtering performance.

- In the coating process with the pulsed DC sputtering method, technological parameters: flow (content) of nitrogen, pulse frequency, temperature of coating sample are technological parameters decisive on the quality of the coating.

- The cleaning process f the substrorate before the coating consists of 2 steps: the first step cleans the surface by chemical method, the second step cleans the surface by high-energy ions.

CHAPTER 3: MATERIALS, EQUIPMENT AND STUDY METHOD

3.1. Materials and equipment used in the study process

3.1.1. Coating materials, samples and equipment

- Material covered includes beer as chromium (99.99%) and N2 gas (99.99%).

- Coating sample is steel SKD11 has the 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%; Size: ϕ15xL5mm, annealed to reach hardness (58$\div$60) HRC, grinded and polished to reach the surface roughness reach Ra <0.02μm.

- Equipment DC B30 is equipment used for the pulsed sputtering process, with the following specifications:

+ Vacuum chambers with 300mm diameter x 500mm height and suction vacuum pumping system to pressure 10-3 Pa;

+ Unbalanced magnetic field sputtering nozzle, 100 mm diameter, 1000 W power;

+ The pulsed DC voltage source with adjustable voltage in the range of (0÷625 V), pulse frequency can be adjusted in the range (0÷ 360 kHz);

+ The sample rotation speed jig can be adjusted in the range (5÷20 v/min);

+ The controlling set of temperature of coating sample can be adjusted in the range (0÷400^{0}C);

+ Control equipment of air flow MFC MKS 2179A, the flow can be adjusted in the range (0 ÷100 sccm).

3.1.2. Equipment for evaluating the properties of the coating

3.1.2.1. Equipment for measuring adhesion (critical adhesion force) of the coating to the substrate and the friction properties of the coating

Measuring adhesion (critical adhesion force) of the coating to the substrate and the friction properties of the coating using equipment UMT - 2, this equipment manufactured by CETR of US (Figure 3.1). With the technical properties of the equipment shown as table 3.1:

Figure 3.1. Laboratory equipment UMT-2

Table 3.1. Parameters of machine UTM - 2

No.	**Parameters**		**Properties**
1	Vertical Positioning System	Greatest cruise, mm	150
		Speed, mm/s	0.01÷10
2	Horizontal Positioning System	Greatest cruise, mm	150
		Speed, mm/s	0.01÷10
3	Greatest load (FZ) put on sample		200
4	Greatest movement length of table bearing sample		10
5	Greatest frequency of the sample table bearing		20
6	Greatest measuring temperature		150

3.1.2.2. Other equipments

- Equipment used to determine the chemical composition of the coating is the scanning electron microscope (SEM / EDX) Jeol JMS 6490/ Jeol/ Japan (Figure 3.2)

- Equipment used to determine the structure of the coating is measured XDR system (Figure 3.3)

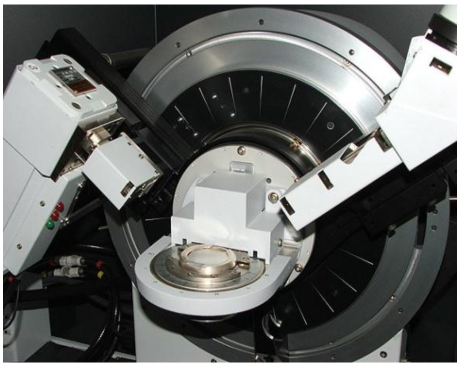

Figure 3.2. scanning electron microscope (SEM/EDX) Jeol JMS 6490

Figure 3.3. X-ray diffraction measurement system (XRD)

- Equipment used to determine the morphology of the surface coating is atomic force microscopy (AFM) type DI 3100 (Figure 3.4)

Figure 3.4. Atomic force microscopy DI 300

- Equipment Dektak 150 is used to measure the thickness of the coating (Figure 3.5), the vertical resolution of $6A^0$, and the thickness from $200A^0$ to 65 µm and the thickness from to 65 micron measured.

Figure 3.5. Dektak 150

Figure 3.6. IndentaMet 1106

- Determining the coating hardness using durometer IndentaMet 1106 manufactured by Buehler-US with with the hardness scale Vickerse with load of 0,01 N to 0,1N, the probe was made from diamonds with spherical form, at the pyramid tip (Figure 3.6).

3.2. Method of evaluating the coating properties

3.2.1. Method of determining the chemical composition

Energy-dispersive x-ray spectroscopy (EDX) method is used to determine the chemical composition of the coating .

3.2.2. Method of determining the structure of the coating

X-ray diffraction (XRD) method is used to determine the structure of the coating.

3.2.3. Method of determining the coating morphology

An atomic force (AFM) method is used to determine the morphology of the coating

3.2.4. Method of determining the coating thickness

Contour measurement method by the probe needles is used to determine the coating thickness.

3.2.5. The method determining the coating hardness

The Vickers hardness test method is used to determine the coating hardness.

3.2.6. Method of determining the adhesion (critical adhesion force) of the coating to the substrate

The incision method is used to determine adhesion of coating to the substrate i. Measurement principle of this method is presented as follows:

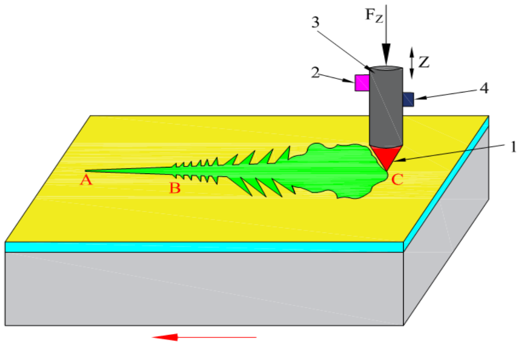

Figure 3.7. Principle of measuring the adhesion of the coating to the substrate

1 - incision nozzle; 2 - sound sensor; 3 - nozzle structure;4 - Position sensor

In this measurement method (Figure 3.7), the sample is placed in the lower and incision nozzle (1) has a radius r0 placed above. On nozzle structure (3) fitted with position sensors (4) (vertical motion control), sound sensors (2) (recording sound emitted during incision nozzle cut into coating samples). Load F_z placed on the incision nozzle is controlled by the vertical force sensor.

- The measurement process is as follows: the incision nozzle is firstly in touch with the sample at point A, the load Fz placed on the incision nozzle is P1 (N), then the incision nozzle laterally move relatively to the coated sample to point C, the distance which the incision nozzle moves in the course of incision process of the coating surface as L = AC (mm). When the incision nozzle moves on AC distance there are 2 events occurred simultaneously:

- The load placed on the incision nozzle increases linearly, to the point C the load placed on the incision nozzle F_Z reaches P_2. Thus the preloading speed is $P_1 – P_2/L$ (N/mm);

- Incision tip moves relatively in the vertical irection into the depth of sample, so when the incision nozzle moves to point C on the sample surface and deep into a piece of sample as L_1 (mm). Therefor, looking at patterns, we see that width and depth of incision track gradually increases from the A to C.

So when the incision tip on the sample relative motion creates a segment AC cuts take away form the coating materials and substrates. The adhesion of the coating to the substrate was evaluated by the critical adhesion force L_C (N). LC value is determined at the position of point B on the incision, which began to appear in the coating peeling or in other words the edge of the incision begins serrated shape at this time, the force value F_Z placed on the incision achieved L_C (N). To determine the exact location of the incision point B on the basis of the audio signal obtained during cut motions incision tip into negative patterns, recorded by a sound sensor mounted on the tip incision, at Point B power sudden sound level changes started to grow up and not stable. Thus, based on the audio signal over time (in the road ditches) obtained from sensors attached to the first sound canal will determine the exact value of the critical adhesion force of the coating to the substrate L_C.

3.2.7. Assessment method of friction properties of the coating

The bearing linear motion model on flat samples is used to evaluate the properties of friction and abrasion of the coating. Measurement principle of this method is presented as follows:

Flat sample is place at the bottom and bearing on top (Figure 3.8). In the process of measuring fixtures for carrying samples relative sliding motion in a straight line horizontal movement of bearings, constant load (F_Z) is set up bi vertical, 2D force sensors mounted on the probe carries ball will determine friction (F_X) generated during sliding bearings on flat samples, the coefficient of friction is defined as the ratio of the distribution formula $\frac{F_z}{F_x}$. Also, in the process of measuring position sensors mounted on ball bearing probe will determine the depth marks on the trail during the bi flat pattern on the sample slide

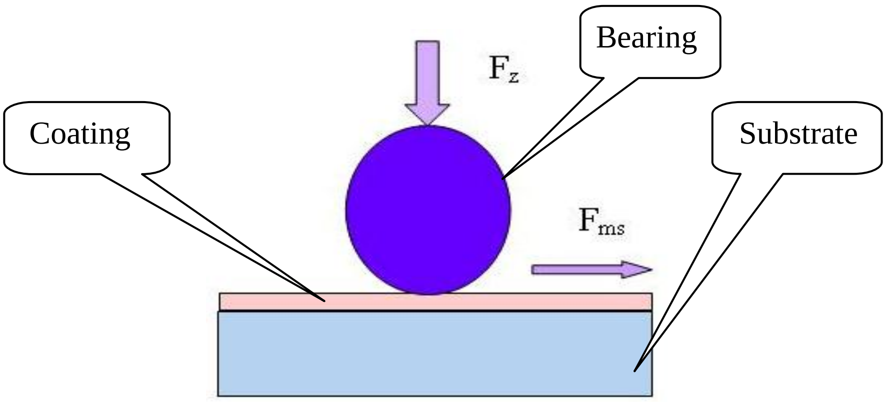

Figure 3.8. *Measurement principle of friction and abrasion in form of reciprocating translation, bearing on flat samples*

3.3. Study method of influence of some technological parameters to the adhesion of the CrN coating with SKD11 steel substrate

3.3.1. Selecting the parameters for the study

The parameters and the value range of the parameters for the study are as shown in Table 3.2.

Table 3.2. The parameters and the value range of the parameters for the study

No.	Parameters	The value range of the parameters for the study
1	Pulse frequency, kHz	50 ÷ 150
2	Nitrogen flow, sccm	4 ÷ 8
3	Temperature of the coated sample, ^{0}C	100 ÷ 300

3.3.2. Study method

3.3.2.1. Encoding and setting experimental matrix

1. Encoding the parameters for the study

2. Setting experimental matrix, choosing the experimental planning method

With the number as 3, the variable as 3 (n = 3) is designed in the Box-Behken planning, the total of experiments is 15.

3.3.2.2. Data processing method

1. Determine the regression model format

The quadratic model is selected to describe the relationship between adhesion force of the coating CrN with SKD11 steel substrate . This model can be expressed as:

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i,k=1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} b_{ii} x_i^2$$

2. Testing the relevance of the model

- Checking the level of significance of the regression coefficients under Student standard;
- Checking the adaptation of standard mathematical model under Fisher standard;
- Checking and evaluating homogeneous variance under Kohren standard.

3. Solving optimal problem

The relationship between technological parameters and objective function can be expressed as:

$$L_C = f(x_1, x_2, x_3)$$

Objective optimization problem to be solved to ensure the desired: Determining the value of x_1, x_2 and x_3 to:

$$L_C \Rightarrow max$$

Conclusion of Chapter 3

- Identifying the properties of the samples prior tocoating, coating materials, equipment and appliances to assess the characteristics of the coating.
- The energy X-ray scattering method (EXD) and the X-ray diffraction method (XRD) are used to determine the chemical composition and structure of CrN coating ; method using an atomic force (AFM) is used to determine the morphology of the coating;   measurement using contour method by needle probe method to determine coating thickness and Vickers method to determine the hardness of the CrN coating .
- The incision method is used to determine the adhesion of the CrN coatings to SKD11 steel substrate. The adhesion of the coating to the steel substrate is determined by the value LC limited adhesion force (N), in which the coating begins to separate from the substrate.
- The bearing linear motion method on flat samples is used to determine the friction properties of the coating. The result of the measurement is the friction coefficient of and the depth of wear marks on the sample.
- The scope of information technology (pulse frequency, nitrogen gas flow temperature and coating samples) are identified to study the impact on the adhesion of the CrN coating to SKD11 steel substrate. The Box-Benhken empirical planning method is applied to study the effects of 3 technological parameters to the adhesion of the CrN coating to the substrate SKD11.

CHAPTER4: DETERMINATING THE INFLUENCE OF SOME TECHNOLOGICAL PARAMETERS TO ADHESION TO THE COATING TO SUBSTRATE, EVALUATING FRICTION PROPERTIES OF the COATING AND APPLICATIONS ON COLD MOLD

4.1. Experimentally determining the influence of some technological parameters to the adhesion of the CrN coating to SKD11 steel substate

4.1.1. Describing the fabcrication process of the CrN coating on SKD11 steel sample

Before coating, the sample is cleaned by chemical method, then the sample is put into the chamber to continue cleaning coated surface over a period of 30 minutes. Then coating with CrN, the parameters of the fabcrication process of the CrN coating are given in Table 4.1.

Table 4.1. The parameters and conditions of the fabcrication process of the CrN coating

No.	Parameters	Value
1	Basic pressure, Pa	$8\ x10^{-2}$
2	Distance between base-stele, mm	100
3	Ar gas flow, sccm	12
4	Sputtering line, A	1
5	Pulse frequency, kHz	50÷150
6	Nitrogen gas flow, sccm	4÷8
7	Temperature of the coating sample, ^{0}C	100 ÷ 300
8	Plating time, min	90

4.1.2. Measuring the adhesion of the CrN coating to the SKD11 steel substrate

4.1.2.1. Conditions for measuring the adhesion of the CrN coating to the SKD11 steel substrate

Measuring the adhesion of the CrN coating to the SKD11 steel substrate was conducted on the device UMT-2 using the incision nozzle with 200μm radius (Figure 4.1). With conditions are measured in table 4.2.

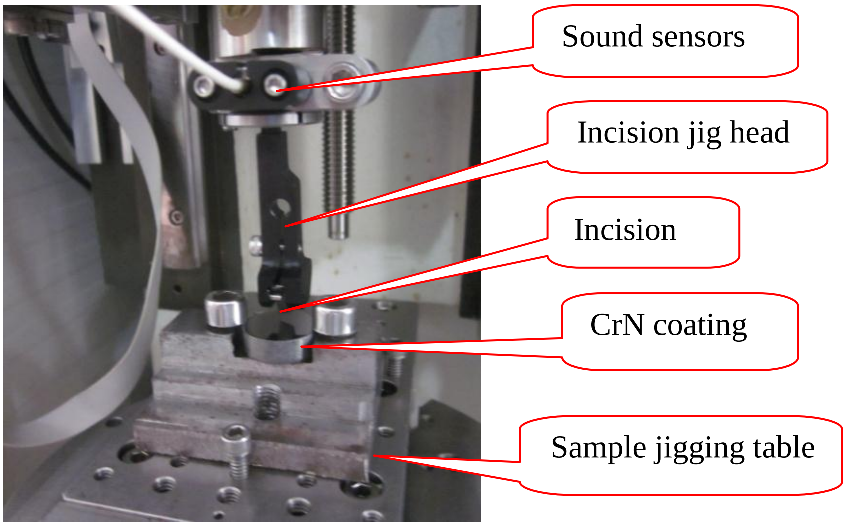

Figure 4.1. Adhesion measurement diagram of the CrN coating to SKD11 steel substrate on equipment UMT-2

Table 4.2. Technological parameters of the adhesion of the CrN coating to SKD11 steel substrate

No.	Technological parameters	Properties
1	Biggest load placed on the head incision F_Z	18
2	Measurement time	30
3	Incision length	5
4	Load speed	$a = \frac{18}{30} = 0,6$

4.1.2.2. Experimental results

1. Measurement results of the critical adhesion force value of the CrN coating to SKD11 steel substrate

After experiments arealready carried out under Box-Behken planning, the critical adhesion force results of the CrN coating are shown in statistical table 4.3.

Table 4.3. Fthe critical adhesion force results of the CrN coating to SKD11 steel substrate

No	**Encoding**			**Actual**			**L_C [N]**
	x_1(f)	x_2(N_2)	x_3(T)	A (kHz)	B (sccm)	C (^{0}C)	
1	*+1*	*-1*	*0*	150	4	200	9.0
2	*0*	*+1*	*+1*	100	8	300	12.0
3	*0*	*-1*	*+1*	100	4	300	11.7
4	*+1*	*+1*	*0*	150	8	200	10.5
5	*+1*	*0*	*+1*	150	6	300	12.2
6	*0*	*0*	*0*	100	6	200	13.1
7	*-1*	*-1*	*0*	50	4	200	9.0
8	*-1*	*0*	*-1*	50	6	100	9.9
9	*+1*	*0*	*-1*	150	6	100	11.5

No	**Encoding**			**Actual**			L_C **[N]**
	x_1(f)	x_2(N_2)	x_3(T)	A (kHz)	B (sccm)	C (^{0}C)	
10	*0*	*-1*	*-1*	100	4	100	9.6
11	*0*	*0*	*0*	100	6	200	12.9
12	*0*	*+1*	*-1*	100	8	100	10.5
13	*-1*	*0*	*+1*	50	6	300	12.2
14	*0*	*0*	*0*	100	6	200	13.3
15	*-1*	*+1*	*0*	50	8	200	9.2
16	*+1*	*-1*	*0*	150	4	200	9.3
17	*0*	*+1*	*+1*	100	8	300	12.3
18	*0*	*-1*	*+1*	100	4	300	11.6
19	*+1*	*+1*	*0*	150	8	200	10.3
20	*+1*	*0*	*+1*	150	6	300	12.4
21	*0*	*0*	*0*	100	6	200	13.1
22	*-1*	*-1*	*0*	50	4	200	8.8
23	*-1*	*0*	*-1*	50	6	100	9.8
24	*+1*	*0*	*-1*	150	6	100	11.2
25	*0*	*-1*	*-1*	100	4	100	9.5
26	*0*	*0*	*0*	100	6	200	13.2
27	*0*	*+1*	*-1*	100	8	100	10.3
28	*-1*	*0*	*+1*	50	6	300	12.5
29	*0*	*0*	*0*	100	6	200	13.2
30	*-1*	*+1*	*0*	50	8	200	9.3
31	*+1*	*-1*	*0*	150	4	200	9.2
32	*0*	*+1*	*+1*	100	8	300	12.2
33	*0*	*-1*	*+1*	100	4	300	11.4
34	*+1*	*+1*	*0*	150	8	200	10.6
35	*+1*	*0*	*+1*	150	6	300	12.1
36	*0*	*0*	*0*	100	6	200	13.3
37	*-1*	*-1*	*0*	50	4	200	8.7
38	*-1*	*0*	*-1*	50	6	100	10.0
39	*+1*	*0*	*-1*	150	6	100	11.4
40	*0*	*-1*	*-1*	100	4	100	9.5
41	*0*	*0*	*0*	100	6	200	13.0

No	Encoding			Actual			L_C [N]
	x_1(f)	x_2(N_2)	x_3(T)	A (kHz)	B (sccm)	C (^{0}C)	
42	*0*	*+1*	*-1*	100	8	100	10.4
43	*-1*	*0*	*+1*	50	6	300	12.5
44	*0*	*0*	*0*	100	6	200	13.2
45	*-1*	*+1*	*0*	50	8	200	9.4

2. Setting regression models of the objective function

Running data analysis program in Minitab software, the results obtained as shown in the photo (table 4.4):

Table 4.4. The results of experimental data analysis

The analysis was done using coded units.

Estimated Regression Coefficients for Lực bám dính giới hạn Lc (N)

Term	Coef	SE Coef	T	P
Constant	13.1444	0.04763	275.949	0.000
x1	0.3500	0.02917	11.999	0.000
x2	0.4042	0.02917	13.856	0.000
x3	0.8958	0.02917	30.711	0.000
x1*x1	-1.5722	0.04294	-36.618	0.000
x2*x2	-2.1306	0.04294	-49.621	0.000
x3*x3	-0.0972	0.04294	-2.264	0.030
x1*x2	0.2083	0.04125	5.050	0.000
x1*x3	-0.4083	0.04125	-9.899	0.000
x2*x3	-0.0667	0.04125	-1.616	0.115

Analysis of Variance for Lực bám dính giới hạn Lc (N)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	101.391	101.391	11.2657	551.68	0.000
Linear	3	26.121	26.121	8.7069	426.38	0.000
x1	1	2.940	2.940	2.9400	143.97	0.000
x2	1	3.920	3.920	3.9204	191.98	0.000
x3	1	19.260	19.260	19.2604	943.18	0.000
Square	3	72.695	72.695	24.2317	1186.63	0.000
x1*x1	1	22.365	27.381	27.3809	1340.84	0.000
x2*x2	1	50.226	50.281	50.2811	2462.27	0.000
x3*x3	1	0.105	0.105	0.1047	5.13	0.030
Interaction	3	2.575	2.575	0.8583	42.03	0.000
x1*x2	1	0.521	0.521	0.5208	25.51	0.000
x1*x3	1	2.001	2.001	2.0008	97.98	0.000
x2*x3	1	0.053	0.053	0.0533	2.61	0.115
Residual Error	35	0.715	0.715	0.0204		
Lack-of-Fit	3	0.119	0.119	0.0397	2.13	0.115
Pure Error	32	0.596	0.596	0.0186		
Total	44	102.106				

Coefficient P value greater than the level of significance α should be removed from the model. For example, components of the regression equation $x_2.x_3$ should be removed from the corresponding P values by 0.115, greater than 0.05. Based on the values in the column "coef", combined with the reference values in column P, ensures that the result of the function regression equation $\mathbf{L_C}$ according to the variables $\mathbf{x_1, x_2, x_3}$ as follows:

$$\mathbf{L_C = 13.14 + 0.35x_1 + 0.40\,x_2 + 0.89\,x_3 - 1.57\,x_1^2 +}$$
$$\mathbf{-2.13\,x_2^2 - 0.09\,x_3^2 + 0.20\,x_1\,x_2 - 0.4x_1\,x_3}$$

It was transferred to the real variable to obtain regression describing the influence of 3 technological parameters (pulse frequency, gas flow temperature nitrogen and coated samples) to the critical adhesion force of the CrN coating to SKD11 steel substrate as follows:

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

From empirical regression showed strong influence to the critical adhesion force of the CrN coating to steel SKD11 substrate covered with the pulsed DC sputtering method that is nitrogen gas flow, followed by pulse frequency and the lowest as temperatures of the coated sample.

3. Solving optimal problem of objective function

Parameters for coating with CrN on SKD11 steel substrate are selected to ensure the highest critical adhesion force of the coating to the SKD11 steel substrate.

Running corresponding optimization functions of Minitab software obtains results as shown in below Figure (Figure 4.2). The results showed that the optimal value of the objective function $\mathbf{L_C}$ is:

L_{CMAX} = 13.96 (N)

Expactation function d = 0,821.

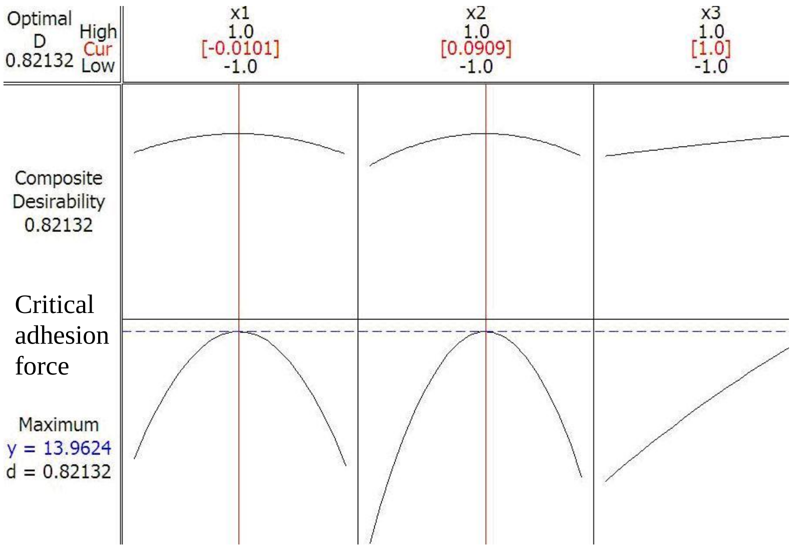

Figure 4.2. The optimal diagram L_C

From the graph determining the technological parameters for the highest critical adhesion force of the CrN coating for SKD11 steel substrate (figure 4.5).

Table 4.5. The value of optimal encoding parameters togenerate the CrN coating gas

x_1	x_2	x_3
-0.01	0.09	1

Transfering to real variables, we get the real value of the reasonable technological parameters used in the coating process as shown in Table 4.6.

Table 4.6. The real value of parameters generated the CrN coating on SKD11 steel substrate

Pulse frequency f [kHz]	Gas flow N_2 [sccm]	Tempeprature T [^{0}C]
99.54	6.18	300

Repeating the experiment with the parameters as shown in Table 4.6 results are obtained the as shown in Table 4.7.

Table 4.7. Adhesion force value of the CrN layer with SKD11 steel substrate when being coated with the optimal parameters

Experiment order number	1	2	3	Average
Critical adhesion force L_C [N]	13,8	13,8	13.9	13,83

Experimental results show the appropriate regression model the stable and rather high adhesion of the CrN coating to SKD11 steel substrate

4.2. Evaluate other properties of the CrN coating

4.2.1. Structure and mechanical properties of the coating

- The CrN coating is made with a volume ratio of Cr and N respectively 77% and 18%.
- The coatings with good crystalline structure, crystal orientation of the coating according to the present primarily with CrN phase has face-centered cubic structure. Spectral peak intensity corresponds to the surface orientation (200) and face (111).
- The size of the particles is 66 nm coating and surface roughness average is 15 nm.
- Coating thickness 3µm.
- The CrN coating has a hardness of 2055 ±10 HV.

4.2.2. Evaluating friction properties of SKD11 steel samples coated and uncoated CrN

4.2.2.1. Friction measurement conditions

Friction and abrasion measurements are made on equipment UTM-2 (Figure 4.3) with experimental measurement conditions measured as shown in table 4.8.

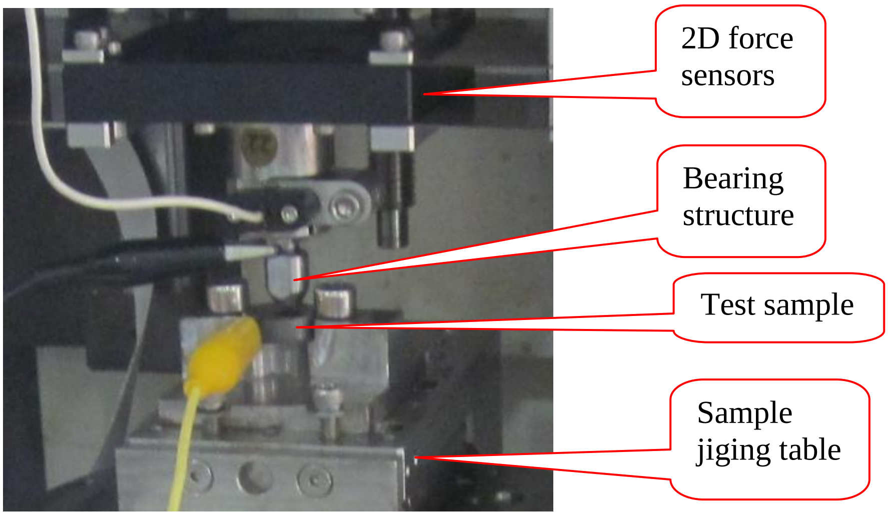

Figure 4.3. Friction measurement diagram and abrision on equipment UMT-2

Table 4.8. Friction testing conditions

Load, N	Bearing		Translational velocity, m/s	Relative humidity, %	Temperature, ^0C	Testing time, min
	Material	Diameter, inch				
5	Al_2O_3	*3/8*	0,1	70 ± 5	24 ± 1	10

4.2.2.2. Measurement results

1. Measurement result of friction coefficient

The relationship between the friction coefficient and the time for CrN uncoated samples and CrN coated samples is stable and highly iterative (Figure 4.4). average friction coefficient value for uncoated sample is 0635 and for coated is 0.3. Thus friction coefficient of CrN coated samples decreased about 2 times than uncoated samples.

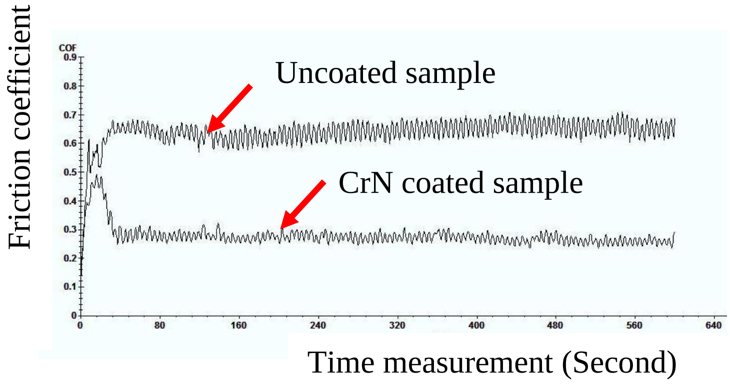

Figure 4.4. Representative friction coefficient of sample CrN coated and CrN uncoated over time

1. Results of measuring the speed trail

Measurement results show that the corrosion rate of uncoated SKD11 steel samples is 7,53x10^6 $(\frac{mm}{s})$ and the corrosion rate of coated SKD11 steel samples is 1,35x10^{-6} $(\frac{mm}{s})$. Such corrosion resistant of the surface of the coated sample is about 6 times higher than uncoated sample

To demonstrate the impact of the CrN coating to the coefficient of friction and wear resistance of SKD11 steel surface sample, must be carried out by analyzing the surface morphology stain worn when using an optical microscope. Through observation of the sample surface uncoated corrosion stains and patterns form government shows no negative phenomena appear serious corrosion on the surface sticky stains and wear and tear of the trace width is much larger than the width stain worn on the negative samples (Figure 4.5, Figure 4.6). This is the explanation of why the sample surface CrN coated friction coefficient and wear rate decreased more than the uncoated samples.

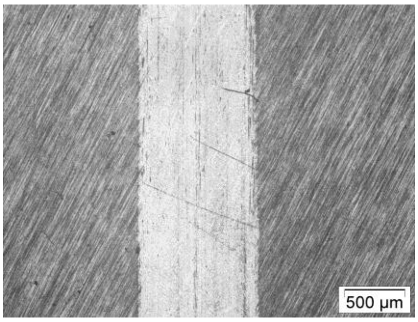

Figure 4.5. Image of abrasion traces and uncoated SKD11 samples

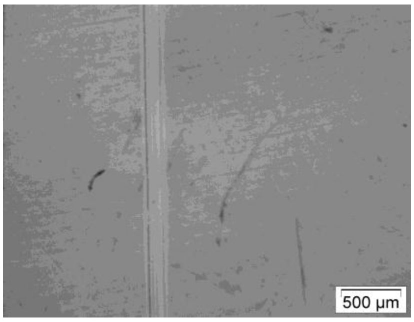

Figure 4.6. Photo of abrasion traces of Crn coated SKD11 steel sample

EDX analysis of wear traces on the surface of the sample with the government to try and tear ascending time: 5 minutes; 10 minutes; 15 minutes, the results showed that% nitrogen content decreasing volume respectively: 17:36%; 15:06%; 14:11%. From analysis of scanning electron micrographs (SEMs) of the EXD analysis shows that the coating is removed from the sample surface using abrasive mechanisms, not the delamination. Therefore, the adhesion between the coating with good substrate.

From the results obtained during the experiments showed CrN coated steel sample surface with a lower coefficient of friction and higher wear resistance, and high adhesion resistant than steel SKD11 uncoated samples. The reason is that the CrN coating on the steel SKD11 achieve the adhesion of the CrN coating for steel SKD11 high substrate, coating crystal structure, small particle size, the proportion of legitimate, reasonable coating thickness and high hardness of the coating. So the technological parameters defined in Table 4.6 is the reasonable technological parameters for CrN-based coating steel SKD11.

4.3. Application of the CrN coating for improving the lifespan of star-shaped mold

4.3.1. The defect phenomenon of star-shaped mold

The star products use on badges, shoulder .... in Army (Figure 4.7) is formed from corrugated piece of 0.3 mm thickness. Creating a star shape using the cold stamping method with mold sets of the steel SKD11 includes punch and pestle (Figure 4.8).

Figure 4.7. Star-shaped stamping products

a b

Figure 4.8. Star-shapped cold mold

a - Pestle; b - Punch

The process of forming a star product is the process of pulling material Baseball billetmortar fills the heart, so the phenomenon of relative slipping between the workpiece and the working surface of the mortar stamping (Figure 4.9), causing the wound stamping and scratches on the surface vegetation and trees leads to defects and unusable stamping. The cause scratching appear this is because when stamping, metal stamping materials mortar sticking to the surface of stamping and forming cumulative abrasive. In the process of stamping while sliding on the surface of the workpiece to form star-shaped bowl, the abrasive particles and scratches on the surface of the product and make the product is broken, and when the grinding particles slough off we scratched mortar onto the surface of cold stamping causes the surface of the mortar worn stamping. Thus, when forming stars with religious material, the main cause of reduced life expectancy mortar stamping (life of dies) by the occurrence of adhesive wear. To overcome this phenomenon in order to increase the life of star-shaped bowl with cold stamping material is religious, it is necessary to reduce friction for cold stamping surface vegetation, increasing the surface hardness of the mortar for cold stamping. Solution was selected as CrN coated onto the surface of the star-shaped bowl with cold stamping base material is SKD11 steel.

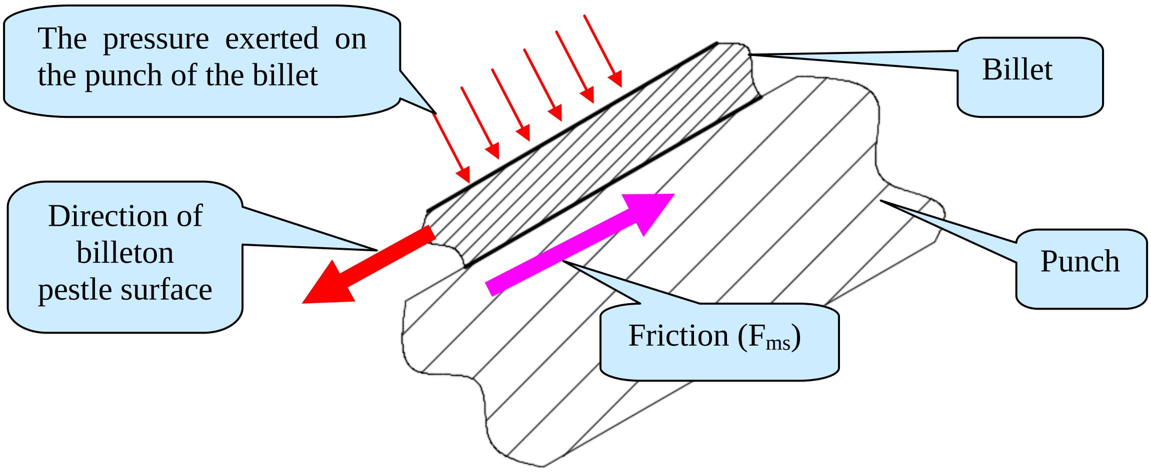

Figure 4.9. The slide of billet on the surface of the punch

4.3.2. Surveying the lifespan of Crn coated star-shaped mold

To survey the effects of the CrN coating to enhance the ability of cold mold life, the subject has been covered with CrN on the working surface of cold stamping mortar with star shaped molding material is SKD11 steel. CrN coating process on the surface layer of the star-shaped bowl of cold stamping is carried out according to the same steps as when coated on SKD11 steel samples, in which the parameters of the coating process on the cold surface of the mold according to the table 4.9.

Table 4.9. The parameters and conditions of the CrN coating process on the star-shaped punch

No.	Parameters	Value
1	Basic pressure, Pa	8 x10^{-2}
2	Distance between base-stele, mm	100
3	Ar gas flow, sccm	12
4	Sputtering line, A	1
5	Pulse frequency, kHz	99,54
6	Nitrogen gas flow, sccm	6.14
7	Temperature of the coating sample, ^{0}C	300
8	Plating time, min	90

Stamping conditions for shaping products on the CrN coated star-shaped punch like the shapping an uncoated punch with Crankshaft MNGLI and without using lubricants.

The testing process shows that the CrN coated cold mold when stamping with corrugated materials with a thickness of 0.3 mm sheet, the process of corrosion of the coating on the surface of the mortar is stamping process abrasive coating flaking not separated. This demonstrates that the adhesion of the CrN coating with good substrate steel SKD11, the government put on mortar satisfactory, the number of processed products on coated CrN mortar hit 15000 units, while the number of products put cold stamping on uncoated mortar at about (7000 ÷ 8000 pcs). Thus, on the surface coated CrN star-shaped bowl of cold stamping significantly improve the longevity of cold stamping mortars. Caused by the cold stamping surface star-shaped bowl covered with CrN, the coefficients of friction on the surface of the mortars fell, leading to reduced ability of the material adhesion to the surface of the mortar die stamping, and surface hardness mortars stamping surface increases, leading to increased resistance to abrasion and scratch resistant working surface of cold stamping mortars. This result demonstrates the government parameters can be applied to actual production, and also shows the influence of the CrN coating lifespan and quality of the cold mold.

Conclusion of Chapter 4

- Applied method Box-Benhken experimental planning method has identified regression function describing the influence of 3 technological parameters to the adhesion of the CrN coating to the substrate SKD11. On the basis of solving the optimal problem, 3 coating technology parameters including pulse frequency of 99.5 kHz, the nitrogen gas flow of 6,18 sccm and the substrate temperature of 3000C for critical adhesion force of the CrN coating to steel SKD11 substrate as the largest (L_c = 13.83 N).

- The steel SKD11 samples coated with technological parameters determined from regression function, the results showed no defect on the CrN coating on steel SKD11 sample, the relatively correct composition of the coating, the coating with crystalline structure oriented mainly in the face (200), 66 nm particle size, coating thickness achieved 3 μm to create teh coating time of 90 minutes and the average hardness of the coating CrN achieving 2055 HV; friction coefficient of coated samples of 0.3; corrosion rate of the sample of $1,35x10^{-6}$ (mm/s)

- Test results in actual production conditions showed that the quantity of products stamping on the CrN coated mold reached 15000 (pieces) in which the uncoated mold only about 7000÷8000 (pieces). The lifespan of the CrN coated cold mold increased approximately 2 times comparedto the uncoated one.

GENERAL CONCLUSION

1. Conclusion

With the aim of creating the CrN coating on SKD11 steel substrate by the pulsed DC sputtering method, then it is applied to enhance longevity and quality of cold mold. The Thesis has achieved the following specific results:

- Selecting 3 technological parameters (pulse frequency, nitrogen gas flow temperature of coated sample) to study the influences of technological parameters of the pulsed DC sputtering method to the adhesion of the CrN coating with SKD11 steel substrate.

- Determining the value of 3 reasonable technological parameters including: pulse frequency of 99.5 kHz, Nitrogen gas flow of 6.18 sccm and coating sample temperature of 3000C. Results achieved in the form of CrN coating steel SKD11 with reasonable technological parameters:

+ Average critical adhesion of the CrN coating to SKD11 steel substrate reaches 13.83 N, the coating with crystalline structure oriented mainly in the face (200), 66 nm particle size, coating thickness achieved 3 um to create teh coating time of 90 minutes and the average hardness of the coating CrN achieving 2055 HV (3 time increse of 3 times compared to the hardness of the uncoated surface);

+ Properties of friction and abrasion of the CrN coating: friction coefficient of coated samples was 0.3 (down approximately 2 times compared with uncoated samples), sample rate of the trail is covered $1,35x10^6$ $(\frac{mm}{s})$ (down approximately 6 times compared to uncoated samples).

- Results of application: Reliability of the CrN coating on the surface of the star-shaped cold mold, the lifespan of Crn coated cold mold increased by about 2 times.

2. Further research directions: Continuing the study of creating multi-layer coating Cr_2O_3/CrN applied in practical production.