KENSUKE UEMURA

DEVELOPMENT AND INVESTIGATION OF BEAM AND PLASMA METHODS FOR IMPROVING THE PERFORMANCE PROPERTIES OF THE PRODUCTS MADE OF METAL MATERIALS

01.04.07 – Condensed matter physics

ABSTRACT
of the thesis for the Degree
of Doctor of Technical Sciences

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The work is performed in NanoCarbon Research Institute Limited
and National Research Tomsk Polytechnic University.

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The thesis is available at Scientific and Technical Library of Tomsk Polytechnic University: Belinskogo Str. 55, Tomsk, Russia.

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Urgency of the theme. The development and approbation of beam-plasma methods of modification of metal articles in industry seems extremely promising. These works are carried out in the scientific laboratories of Russia, Japan, USA, Germany and some other countries for the last 30 years. In general, to modify the materials, pulse and continuous sources are used of plasma, electron and ion beams, and laser emission. These investigations have both fundamental significance from the viewpoint of studying the substance behavior and occurrence of physical and chemical processes under extreme conditions and practical significance based on scientific and technical justification of processes. In the given papers, there are the investigation results, which are based on the use of electron beams of microsecond duration, plasma methods for coating in modification, improving properties exploitation of the articles made of metal materials, as well as development and scientific-technical justification of the corresponding technological processes for series of industry branches, medicine and etc. The **relevance** of the given studies is of high practical significance. It is based on the possibility of increasing the service properties of the corresponding products, and decreasing the materials consumption.

Practical realizations of these approaches are still related to the necessity to solve whole set of technical, technological, methodological and methodical problems, which are also reflected in the papers.

The investigation **purpose** is to develop scientific and methodical fundamentals, scientific and technical justification for the practical application of beam-plasma technologies in solving some critical tasks of medical instrumentation and industrial products.

The methods for the investigation and development of technological processes are based on the use of:

- laboratory and industrial electro physical setups, designed for the generation of low energy pulse electron and ion beams,
- magnetron and arc plasma sources for forming of the functional coatings,
- glowing cathode plasma sources for nitriding,
- analytical equipment, including scanning and transmission electron microscopy of high resolution, Raman scattering spectrometry, photoelectron and X-ray spectroscopy, Auger spectroscopy, time-of-flight mass spectrometry, metallography and others
- industrial test equipment,
- theoretical models describing the motion of electrons in electromagnetic fields, plasma generation, and chemical reactions in plasma.

The scientific novelty of the thesis are defined by the following results:

1. The preliminary film deposition of boron nitride in the steel substrate of SKD11 with the further ion implantation leads to cubic boron nitride formation

with the size of the particles of about 30 nm and the correlation of the phases of cubic and hexagonal boron nitride 83:17.

2. During ion implantation of nitrogen into the steel SKD11, the hardness increases more than during implantation of the argon with the friction coefficient decrease by 3 times and 2 times correspondingly.

3. During the treatment of the alloy SKD11 by plasma generated in nitrogen, the formation of the composition Fe_4N occurs in the depth up to 100 μm which results in the hardness increase from 870 kg/mm^2 to 1750 kg/mm^2.

4. For the first time the technological process of service properties improvement of press-forms and forming dies made of super hard alloys is developed and implemented due to the pulse electron beam treatment combined with the deposition of diamond like carbon coatings.

5. The technological process of service properties improvement of extrusion dies made of super hard alloys is developed using the pulse electron beam together with copper sedimentation and additional polishing of the dies in a vacuum discharge when the treated article is under negative potential.

6. The irradiation modes of the pulse electron beam increasing the corrosion properties, bio-compatibility, and the surface roughness of the metal articles applied in medicines: stents, nickel-titanium guide wires, hip and knee bone joints, precious metal dental prosthesis, titanium alloy fixators for the broken bones are determined for the first time.

7. It was proved that the particles of the nano-onions and nano-diamonds with the diameter more than 90 nm can be synthesized from graphite by means of pulse electron beam with the energy 30 keV and the currency density more than 17 kA/cm^2 using copper plasma as the catalyst. The mechanism of nano-onion forming is based on the destruction of the carbon bonds, shifting of carbon atoms and electron beam heating. The target heating temperature under the action of the pulse electron beam must satisfy the temperature of graphite evaporation.

The practical significance of the papers and the relevance are approved by the practical use of the results of the work in numbers of industrial and medical products. The findings applied: improvement of operational properties and sharpening of razor blades, finish polishing of dies by electron beam products after the electrical discharge machining, improvement of corrosion properties, bio-compatibility, and surface roughness of numbers of products used in medicine.

The personal contribution of the author. The thesis is the culmination of the years of research conducted in the NanoCarbon Research Institute Limited and High-Voltage Research Institute at TPU with direct participation and under the direction of the author. The author has made a decisive contribution to the formulation of the problems and choice of the directions and research methods.

Some of the results were obtained with the number of co-authors indicated in the list of publications. Comprehensive studies of the process of nitrogen and argon implantation in the SKD11 steel and the formation of carbon structures were conducted independently by the author. The author has put forward the defending scientific statements, made conclusions and given recommendations based on research findings. The discussion of the problems of research, methods of their solution and the results was carried out jointly with colleagues.

The main points for the defense:

1. CN_X coatings at $0 \le X \le 0.5$ obtained by the plasma chemical method during the arc evaporation of graphite in nitrogenous plasma contain the mixture of two types of particles: diamond-like and $CN_{0.5}$ particles with the bonds Sp^2.

2. Ion implantation of nitrogen into the steel *SKD11* results in the hardness increase and the friction coefficient decrease by 3 times correspondingly.

3. The phase of cubic boron nitride in the form of nanosized particles during ion implantation can be formed in the surface coating of SKD11 with the pre-deposited film of boron nitride.

4. During the treatment of the alloy *SKD11* by plasma generated in nitrogen, the diffusion depth of nitrogen reaches 100 μm with the hardness increase up to 1750 kg/mm^2.

5. Pulse electron beam application combined with the deposition of diamond like carbon coatings results in service properties improvement of press-forms and forming dies made of super hard alloys.

6. The service properties of extrusion dies made of super hard alloys can be improved using the pulse electron beam together with copper sedimentation and additional polishing of the super had alloy surface in a vacuum discharge.

7. The improvement of the corrosion properties, bio-compatibility, and the surface roughness of the metal articles applied in medicines: stents, nickel-titanium guide wires, hip and knee bone joints, precious metal dental prosthesis, titanium alloy fixators for the broken bones is achieved using the pulse electron beam treatment.

8. The method for the improvement of the shaving blades properties and edge-sharpening providing the rounding-off radius of the blade less than *300* Å is achieved due to plasma nitriding.

9. The particles of the nano-onions and nano-diamonds with the diameter more than *90 nm* can be synthesized from graphite using pulse electron beam with the energy *30 keV* and the currency density more than $17\ kA/cm^2$ using copper plasma as the catalyst. Synthesised nano-onions are stable in the environment not less than two years. The heating temperature of the graphite under the action of the pulse electron beam must satisfy the temperature of graphite evaporation.

The approbation of the investigations. The main results of the work were reported and discussed at 19 international scientific conferences in Russia, Japan, Israel and the USA: the National Meeting of Japan Society of Electrical-Machining Engineers, 2002, Saitama, Japan; 6th International Conference «Modification of Materials with Particle Beams and Plasma Flows», 2002, Tomsk, Russia; the International Conference on Leading Edge Manufacturing in 21st Century, 2003, Niigata, Japan; Meeting of the Japan Society of Electrical-Machining Engineers, 2003, Tokyo, Japan; Mitsubishi Materials Tools Meeting «Surface Treatment and Thin Film Technologies», 2003, Akashi, Japan (invited lecture); the 18th American Society for Precision Engineering Annual Meeting, 2003, Washington, USA; the 10th Japan Society for Precision Engineering, 2003, Japan; «Combined Surface Modification», Hiroshima University, Japan, 2003 (invited lecture); the 3rd Japan Society of Electrical Machining Engineers, 2004, Japan; 7th International Conference «Modification of Materials with Particle Beams and Plasma Flows», 2004, Tomsk, Russia; 40th Electric Processing Conference "Thin films, and materials modification with its application», 2005, Okayama, Japan; 8th International Conference «Modification of Materials with Particle Beams and Plasma Flows», 2006, Tomsk, Russia; 9th International Conference on Nano Carbon & Nano-Diamond «Updated report on Conversion of Nano-Carbon to Nano-onion and Bucky-diamond with Low Energy Electron Beam Irradiation», 2006, Ioffe Physico-Technical Institute St. Petersburg, Russia (invited lecture); the 3rd NEDO/ISTC Nano-carbon/Nano-diamond Workshop «Pulsed Power Discharge: A New Method for Preparation of Nano-particles Effect of Ultra Violet irradiation for Surface Treatment of PCD and DLC Films», «Progress in the Macroscopic Production of Carbon Nano-Onion Particles», 2007, Dead Sea, Israel; 9th International Conference «Modification of Materials with Particle Beams and Plasma Flows», 2008, Tomsk, Russia; 41st Electric Processing Conference «The functional highly advanced study group of an artificial joint «Hand polish finish with electron beam irradiation of bio-mechanical material (titanium alloy)», 2009, Tokyo, Japan.

Publications. The main points of the thesis are published in 23 printed works, in the journals from the list of journals recommended by WAK, Russia.

The structure and the scope of the thesis. The thesis includes introduction, 3 Chapters, references including 146 items. The material is presented by 234 pages, contains 291 figures and 58 tables.

CONTENTS OF PAPER

In Introduction the topicality of the thesis theme is justified, the scientific problem, the purpose and the scientific tasks being solved in the thesis are determined. The scientific novelty, practical significance of the work and the main points for the defense are stated. The characteristic of the publications on the theme of the thesis, the structure and the volume of the work are given.

In Chapter 1 «Deposition of Functional Coatings» the results of the investigation of hydrogen-free diamond like carbon coatings and the method of their formation with the help of the pulse arc sputtering of graphite are summarized.

It was revealed that the growth of the diamond-like carbon film occurs in the presence of ions C^{+} that is why it is not mono-crystalline. The diamond-like carbon film contains carbon cluster compounds of both Sp^3 and Sp^2.

When using the diamond like carbon films, the main problem is high internal stress σ_0, which is caused by its separation from the sublayer and increases the friction factor. To solve this problem, the nitrogen ions were implemented into the diamond-like carbon structure. The CN_X coatings with the nitrogen concentration $0 \le X \le 0.5$ are the mixture of amorphous particles, with significant concentration of nitrogen. It also indicates the presence of the Sp^3 bonds. In the given chapter, the dependences of mechanical and tribological properties of CN_X coatings on nitrogen concentration are represented. The growth scheme of diamond-like carbon film is represented in Fig. 1.1.

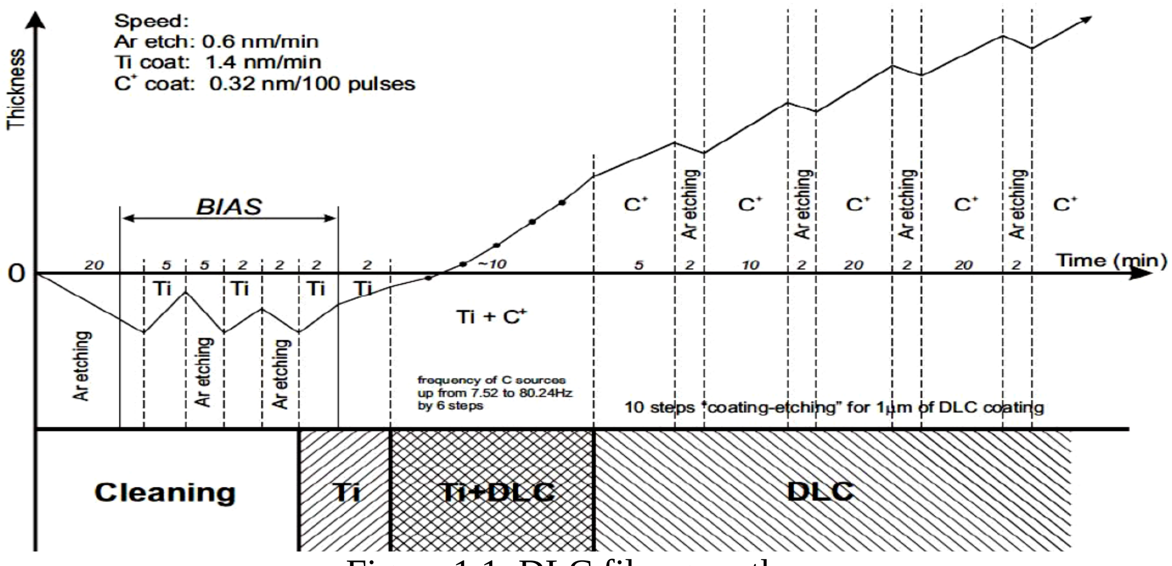


Figure 1.1. DLC film growth

During obtaining the diamond like carbon film by arc spattering of the graphite, carbon content with Sp^3 structure is about 70%. This was approved by three kinds of measurements:

1. Auger electron spectroscopy with the electron energy calibration of the energy level by *C1s* data of X-ray photoemission spectroscopy;
2. X-ray photoemission spectroscopy of valence bands;

3. Electron energy loss spectroscopy *C1s*, on pyrolytic graphite with an ordered orientation and on diamond.

Also we revealed weak dependence of the peak position of "Raman spectrum" on the annealing temperature and the uncertainty in the ratio of the amplitudes of the peaks. These results correlate with the findings of the other authors on the problems of using the Raman spectroscopy for the analysis of diamond like carbon films. Destruction of the structure of diamond like carbon films when heated to 150°C leads to the increase in the ratio of carbon structures Sp^2/Sp^3 to the unit and, as shown by Auger electron spectroscopy, before the disappearance of Sp^3 structure (which is characteristic to nano-scale forms of carbon) at 300° C . It is proof of the non-equilibrium state of carbon atoms in diamond-like carbon structure.

The value of internal stresses, which determine the strength and other characteristics of the thin films, was determined by measuring the density of lattice dislocations and their removal. In this paper, in addition to the internal stress, we measured: the thickness of diamond-like films by the nuclear-physical method; thermal conductivity; coefficient of linear thermal expansion. Micro-hardness *HV* was 10.17 GPa. When using the needle bearing with a polyolefin lubricant, the coefficient of friction μ at a rotation speed above 200 rpm did not exceed 0.01 (Fig. 1.2).

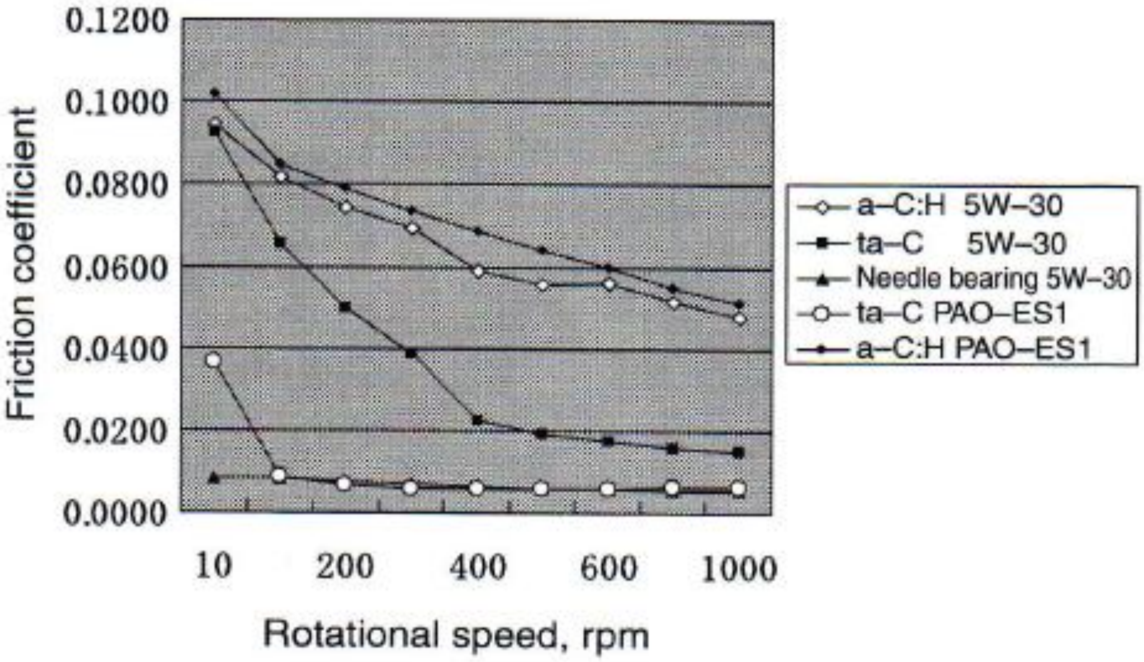


Figure 1.2. The dependence of the friction coefficient on rotational speed

If the combination of aluminum (rod) and amorphous carbon (disc) are used, the wear of diamond-like coatings used as a dry lubricant is 10^{-8} mm^3/N·m, that is much less than 10^{-6} ~ 10^{-7} mm^3/N·m for the materials on the basis of the graphite and Teflon. It indicates that diamond like carbon coatings are applied in friction vapors and are wear-resistant material.

To determine the structure of diamond-like carbon coatings, we used the methods of X-ray photoelectron spectroscopy and X-ray Auger spectroscopy.

Photoelectron and Auger investigations were made by means of non-monochromatic $Al\ K\alpha$ X-ray source (1486.6 eV).

The spectroscopic methods used in the paper are applied for the following thicknesses:

1. Auger spectroscopy - *N(E)*, which is sensitive to Sp^2, Sp^3 bonds, at the depth of two monolayers;
2. X-ray electron spectroscopy of valence bonds, which is sensitive to Sp^2, Sp^3 bonds at the depth of ten monolayers;
3. Optical spectroscopy of electron energy losses - C1s, which is sensitive to Sp^2, Sp^3 bonds at the depth of two-ten monolayers;

We offered the model to determine the combined hardness of the film and the substrate:

$$Hc = 3\left(\frac{t}{d}\right)\left(\frac{Hf}{Ef}\right)^{\frac{1}{n}} (Hf - Hs) \tan^{\frac{1}{3}} \theta + Hs \qquad (1),$$

Where, *Hc* is a combined hardness; *t* is the thickness of the film; *d* is the diagonal of Vickers indentation; *Hf* ; *Hs* are the hardness of the film and the substrate; θ is a half angle of the indentation; *n* is the value chosen by experiment.

The main conclusions of the Chapter 1:

1. Diamond like carbon films of the carbon are not mono-crystalline and contain Sp^3 and Sp^2 bonds. The irradiation of the films by the electron beam leads to the structural transition to graphite, that is determined by the Raman spectroscopy method;
2. A study of the structure of the coatings CN_X with nitrogen concentration $0 \le X \le 0.5$ revealed the presence of mixture of two types of amorphous particles: diamond like domains with utmost concentration of nitrogen (that admits the existence of Sp^3 bonds to 10%), and particles C_2N with Sp^2 bonds;
3. With the help of Auger spectroscopy of the carbon, it was found out that the content of Sp^3 in diamond like carbon structure obtained by a pulse arc spattering of graphite is 70%;
4. The diamond-like carbon films deposited at low substrate temperature *(f* = 1 Hz, T_s ~ 70 °C) have markedly higher H_f values than those obtained at higher substrate temperature (f=20 Hz, T_s ~300 °C);
5. Annealing at a temperature above 500 °C leads to a significant decrease in adhesion;
6. When using the needle bearing with a polyolefin lubricant, the coefficient of friction μ at rotational speed above 200 rpm did not exceed the value of 0.01.

In Chapter 2 “Materials Modification” the treatment of materials by electron beam, and plasma ions was studied. In the first case, a special attention is paid to the transfer of electrons to the treated materials, in the second case – the ion implantation.

The targets with a layer of hexagonal boron nitride (*hBN*) were subjected to the ion implantation. The formation of cubic boron nitride in steel *SKD* was determined by X-ray diffraction.

The relevance of the study is the necessity to increase the service properties of the work pieces.

The setup with the cathode operating on the basis of explosive electron emission is shown in Fig. 2.1.

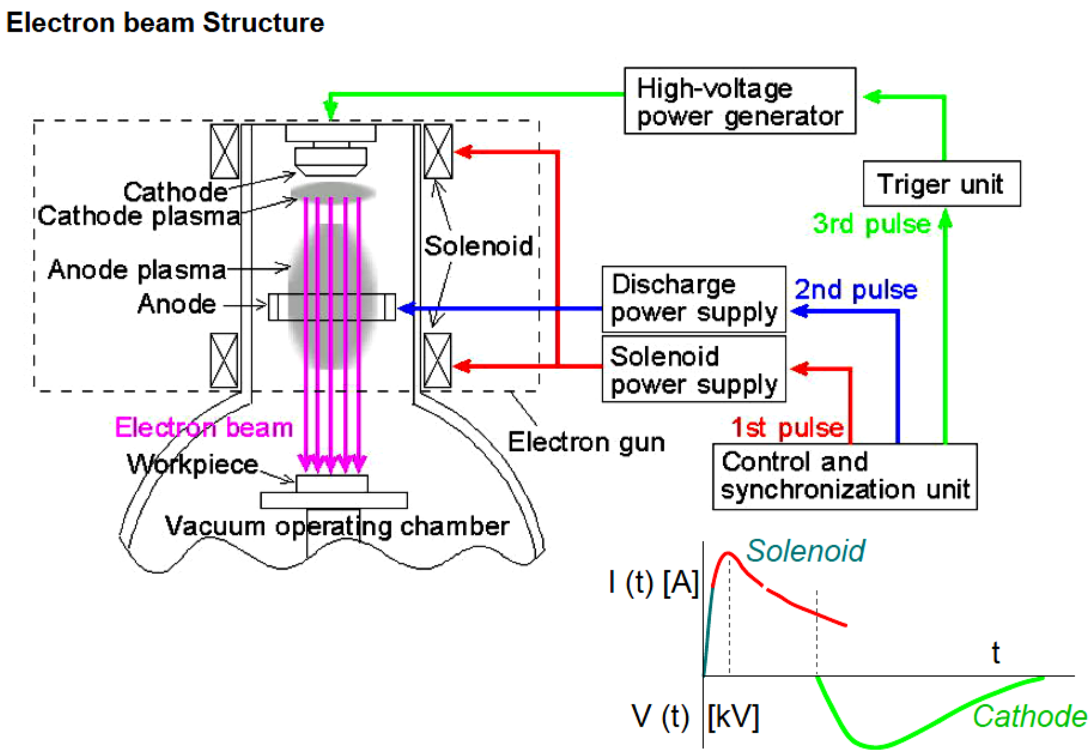


Figure 2.1. The scheme of the setup intended for generation of the electron beam [1]

For the numerical calculation of electron transfer and determination of the parameters of the electron beam, acting on the target, the theoretical models have been developed, that included the following equations:

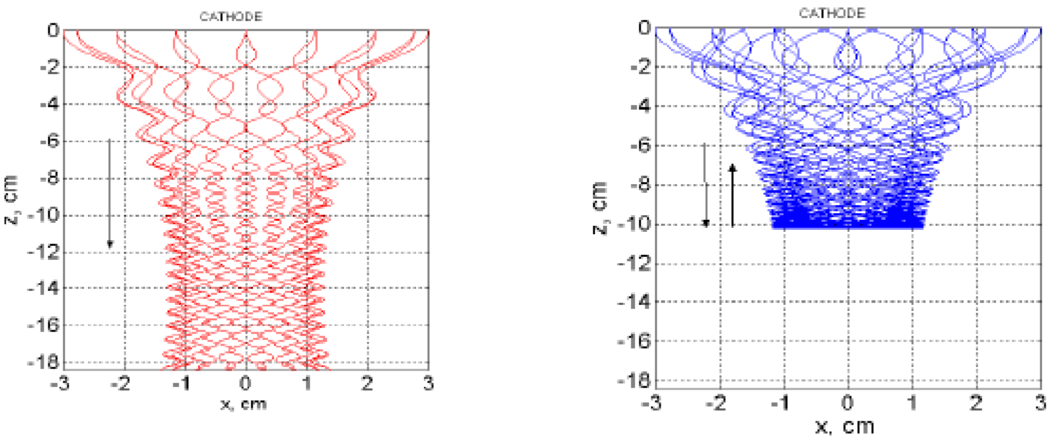
1. Maxwell's equations - to describe the electromagnetic fields to be solved by the PIC (particle-in-cell) method;
2. equations describing the motion of electrons in electromagnetic fields;
3. equations that take into account the generation of plasma and initiating the electric current in the plasma formed in the working gas (*Ar*).

In addition to the system of Maxwell's equations, the Poisson equation was used. The system of these equations was solved numerically by two methods - the "particle in cell" and "the envelope line". In the code of the “particle in cell", the geometry and number of particles depend on the beam geometry and parameters (10000 particles) and in the method of “the envelope

[1] G.E. Ozur, D.I. Proskurovsky, V.P. Rotshtein and A.B. Markov Production and application of LEHC e-beams // Laser and Particle beams (2003), 21, 157-174

line”,the calculations of the curve of a large number of electrons in different conditions took place.

The trajectory of the electron beam drift taking into account the neutralization of electric charge is shown in Fig. 2.2.



(a) (b)

Figure 2.2. (a) Electron beam compression; (b) Pinch effect

Based on numerical results, a model of energy transfer can be represented as follows. When the plasma density $n_p \geq 9 \cdot 10^{11}$ cm^{-3}, the electron beam can be focused on the target by applying an external magnetic field of special configuration. The beam with an initial radius of 3 cm can be focused to ~ 1 cm. The own magnetic field and recording the distribution of the initial angle velocities of electrons reduce the efficiency of energy transfer by the beam up to 30%. This is acceptable for treatment of the material by a focused beam.

An additional coil of the electromagnetic field makes it possible to move the magnetic field and control the radius of the electron beam on the target. Energy carried by the electron beam was measured by a calorimeter with preliminary calibration (Figure 2.3).

To treat the work pieces by plasma ions, we used a plasma source with a glowing cathode (PINK) [2] with the following parameters:

1. Filament current of the cathode	100-150 A
2. Filament voltage of the cathode	~ 4-12 V
3. Discharge current	1-150 A
4. Discharge-operation	30-60 V
5. Magnetic-core current	0.4-0.8 A

[2] The hollow cathode system know as DUET® or PINK® by IHCE at RAS – Tomsk headed by N. Koval.

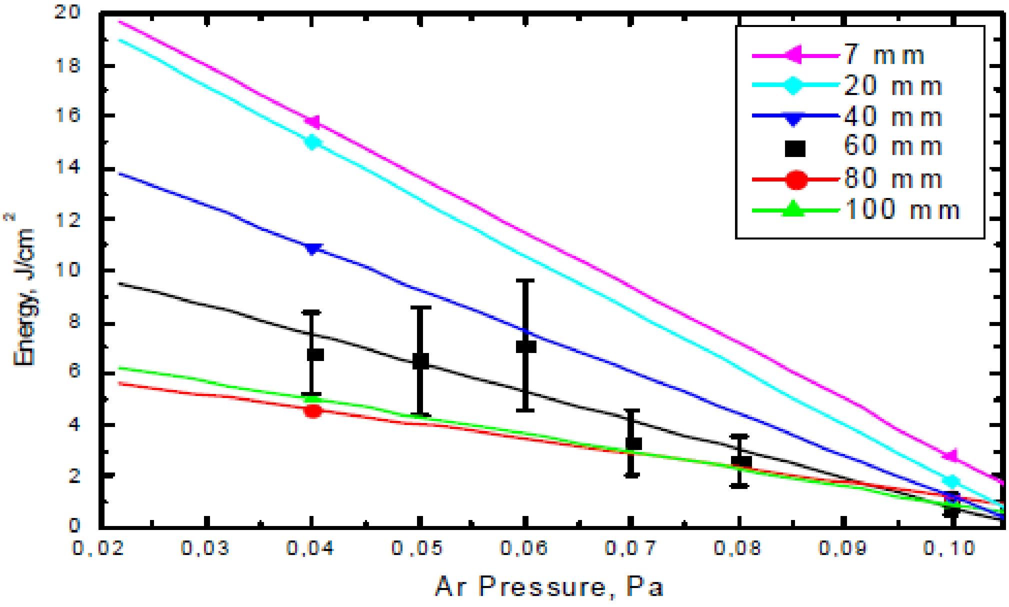
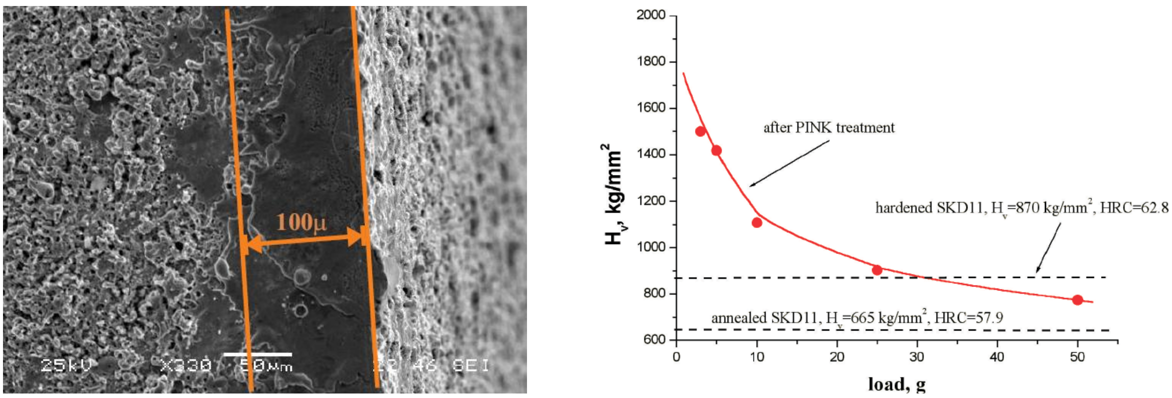


Figure 2.3. Dependence of energy of the electron beam on argon (the distance from electron gun to the calorimeter is given in Figure)

Diffusion zone by Nitrogen is observed around 100μm in case of SKD11. (Etched with 4%HNO_3+C_2H_5OH) HV increased from 870kg/mm^2 (substrate SKD11) to 1750 kg/mm^2 at the top surface due to generation of the inter-metallic compound Fe_4N (Fig. 2.4).



(a) (b)

Figure 2.4. (a) Cross section after N_2 ion implantation; (b) Surface HV after the treatment

The generation of the ion beam was ensured by the use of the hollow anode with the applied positive potential in several kV. The scheme of the Ion Gun [2] is demonstrated in Fig. 2.5.

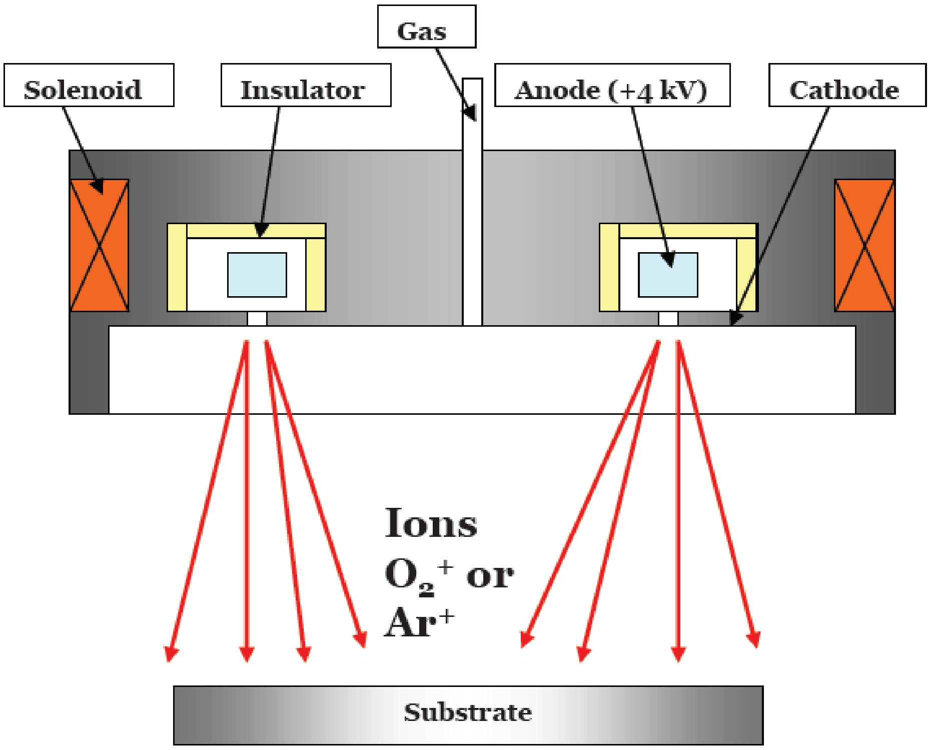


Figure 2.5. Scheme of Ion Gun

The current of the ion beam depends linearly on the plasma density to the density 10^9 cm^{-3}. Besides IB linearity, it was observed the plasma density 10^{10} cm^{-3} by Ion Beam and 10^{10} cm^{-3} by arc discharge due to the space charge layer dimension that is inversely proportional to the plasma density. The relation is illustrated in Fig. 2.6.

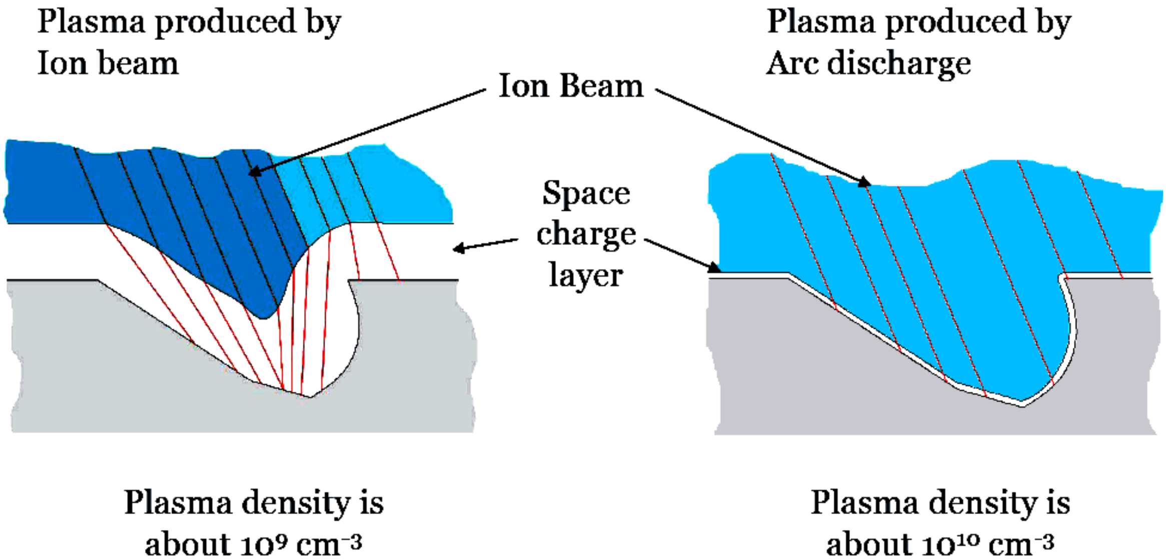


Figure 2.6. Space charge layer dimension is inversely proportional to the plasma density especially in case of complex shape

For the technology of treatment of metal products, a combined system for the generation of electron and ion beams has been designed as shown in Fig. 2.7.

An electron beam generated in the source with a hollow cathode was typically used for heating and annealing of work pieces

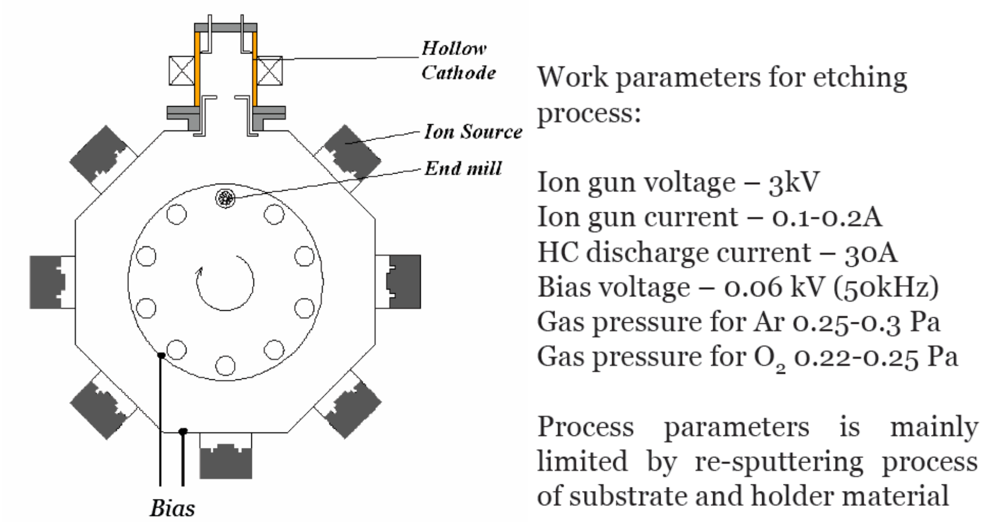


Figure 2.7. Combined system of Ion Guns and Hollow Cathode. The main parameters are shown in right sides

Ion implanter (Fig. 2.8) with the spattering of the target by plasma ions formed in the Penning discharge was designed to improve the coating adhesion to the substrate [3]. Implantation current is 20~30 mA/cm^2 at accelerating voltage up to 30 kV.

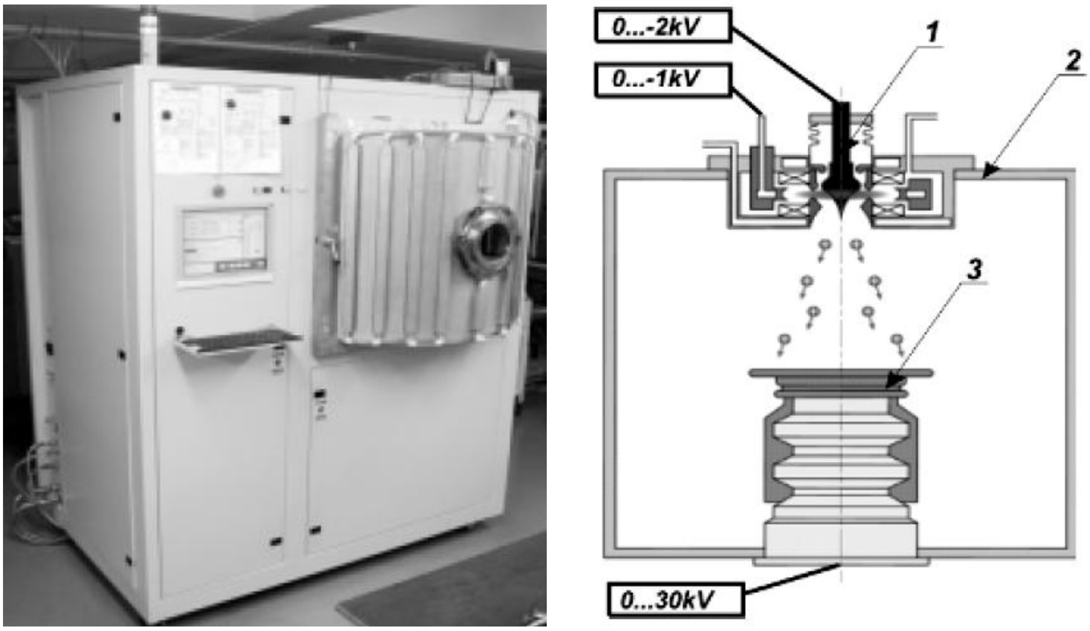


Figure 2.8. The picture of the setup for the ion implantation and the scheme the setup. *1* - Ion gun on the base on target sputtering by Penning discharge plasma, *2* – vacuum chamber, *3* - samples holder on thebase insulator

For both the substrates of WC-9%Co and Steel SKD11, the implantation properties were examined with TiB_2+N_2 and +Ar carrier implantation during ion

[3] V.V. Brukhov, Tools durability increasing by means of ions implantation, Tomsk, NTL, 2003.

beam treatment, which was formed in the setup shown in Fig. 2.9. Anode material is TiB_2, the chamber was filled with nitrogen mixed with argon.

If the hard alloy products are treated (*WC*, 9% *Co)*, the use of *Ar* is more effective than N_2. The friction coefficient in the case of argon is decreased by 30% and depend on the implanted doze, but it increases when using N_2. It happens due to the formation of nitrogen compounds. The value of hardness in these cases did not reveal significant difference between the use of N_2 and *Ar*.

During treatment of steel *SKD11*, the boundaries of the grains become more significant if increasing the dose, if we use *Ar* and N_2. The hardness significantly increases when using N_2. The changes in the wear factor were not significant both for *Ar* and for N_2.

Generation of cubic Boron Nitride (*cBN*) inside the substrate materials with hexagonal Boron Nitride (*hBN*) target was determined with XRD on steel (*SKD11*) and on Cupper plates. The crystal size is calculated with Scherer equation: $L = K\lambda / (\beta_0 \cos\theta B)$. On both samples, the generation of *cBN* was confirmed with its size about 30 nm. With the above results, the generated ratio of *cBN* and *hBN* is understood as *cBN*: *hBN* = 83:17.

The main conclusions of Chapter 2:

1. In the case of materials treatment by electron beams:

1.1. When the plasma density is $n_p \geq 9{\cdot}10^{11}$ cm^{-3}, the electron beam can be focused on the target by applying an external magnetic field of a special configuration. The beam with an initial radius of 3 cm can be focused to ~ 1 cm;

1.2. The peculiar magnetic field recording and the initial angle distribution of beam electrons reduce the calculated efficiency of the beam energy transfer up to 30% from the initial one.

2. In case of plasma material treatment nitrogen diffusion depth is about 100µm in case of *SKD11*, the compound Fe_4N formation results in considerable hardness increase from 870kg/mm^2 to 1750 kg/mm^2.

3. The installation of the combined treatment of the products by the ion and electron beam was realized.

4. Ion implantation of *Ar* in hard alloys based on tungsten carbide is more effective than N_2 implantation at low doses. The friction coefficient in case of *Ar* use decreases 30% in comparison with N_2. This is connected with the formation of nitrogen compounds. The hardness in this case almost doesn't change. Argon use also leads to the significant improvement of the tribological properties of the surface. During the energy density increase the boundaries of the grains become more significant when using both *Ar* and N_2.

5. During ion implantation into steel SKD11 the hardness is considerably increased when using N_2. The friction coefficient decreases 3 times and twice in case of *Ar* use. On both samples SKD and copper, the generation of cubic Boron Nitride (*cBN)* with the grain size of about 30 nm. was confirmed, the ratio of *cBN* and *hBN* (hexagonal) was 83:17.

In Chapter 3 "Application of Beam-Plasma Technologies" the fields of applications of the developed technologies in the following areas are stated:

1. *Hardening of the shaped punches.* Limited lifetime of the shaped punches is due to the formation of cracks on the surface during the electric discharge machining of the working relief forming. Their appearance is connected with the diffusion of cobalt in the surface layer. A longer service life is achieved by using diamond like carbon hard coatings which reduce the friction. The results of finite elements analysis show that in the case of formation of the low roughness surfaces the steel satisfies the conditions of plasticity. Brittleness and hardness depend on the cobalt content and the uniformity of WC particles distribution. The use of the electron beams, reduce the roughness of the shaped punches. Since this treatment is not applicable to polycrystalline diamond, the diamond like carbon coatings are deposited after processing by electron beam.

2. Extrusion dies. The electrical discharge treatment allows for an increase in resisting to the cracks propagation caused by the electron beam irradiation. A significant roughness of the processing surface can be reduced by the pulsed vacuum breakdown, when the work piece is the cathode. Explosive electron emission which is mainly formed on the micro protrusions of the cathode surface leads to decrease in surface roughness (Fig. 3.1). The cracks were eliminated by alloying copper diffusion by means of “SOLO” set-up for electron irradiation. The results of both the scanning electron microscopy and the electron microprobe analysis show that the molten copper penetrates into cracks and smoothes the surface. WC-Cu (Cu bonded with WC) has 30-60% higher resistance wear than the WC-Co (Co bonded with WC).

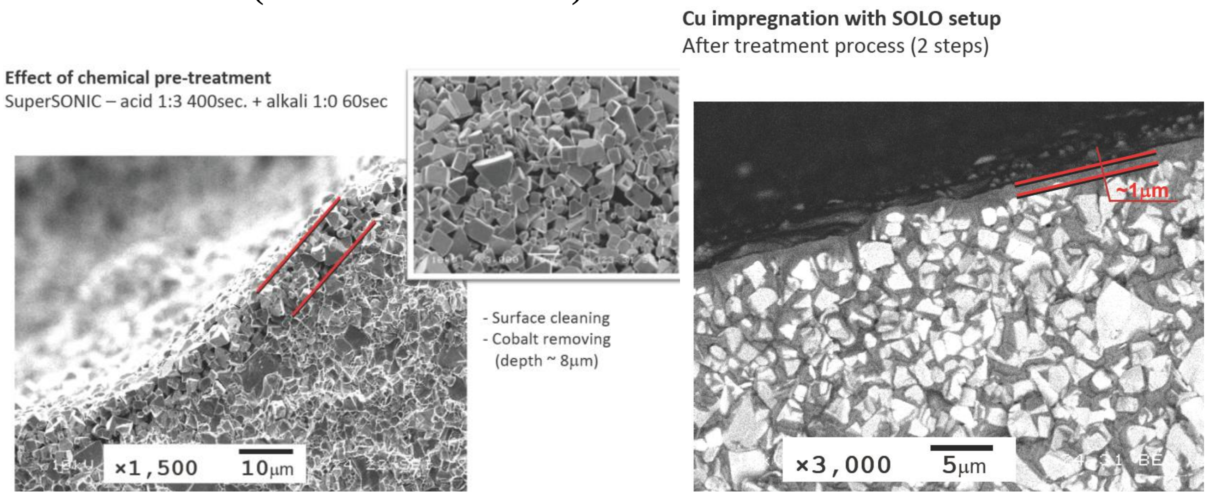


Figure 3.1. The microstructure of the die filter after the deposition of copper

The wetting angle of oxygen-free copper on the surface of WC at the temperature of MP +50 K is 0° (±5°), so the molten copper is almost completely covers the surface of the WC substrate. The WC-Co dies with the surface covered with copper show lower coefficient of friction during operation of extrusion. When copper plating with a thickness of 0.1 μm is coated by the deposition of Cu vapor on the WC, the surface abrasion is double reduced. In this case, cobalt was removed from the WC-Co dies surface by means of the acid, and oxides were eliminated by the "Murakami agent" combined with the simultaneous ultrasonic irradiation. The “SOLO” installation was used for the evaporation of the thin copper plates located under the extrusion dies and for the filters used for purification of the diesel exhaust engines. Its use has led to a decrease in the friction coefficient and an increased durability of the extrusion matrix.

3. *Molds.* When using the SKD11steel as the molds, the reason of the dints formation is Cr, which is contained in the M_7C_3carbides. In the SKD61steel, the reason of dints is the insoluble carbide metal (Fig. 3.2).

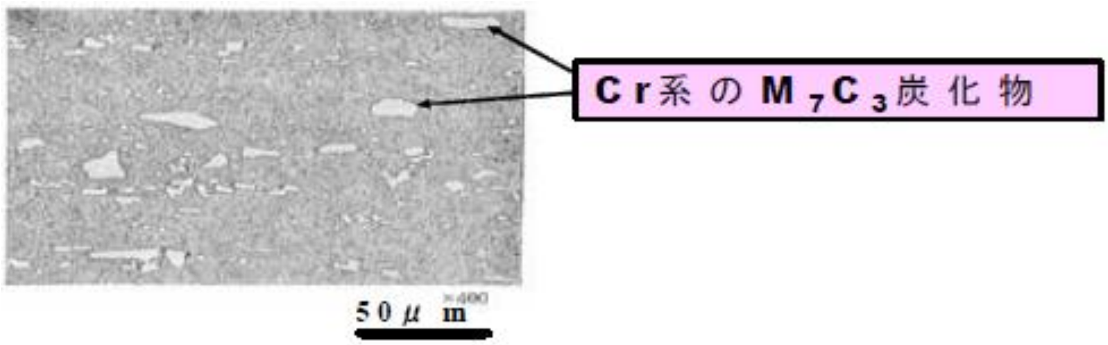


Figure 3.2. The microphotograph of the SKD11steel. The arrows indicate the inclusion of metal carbide with chromium

In this regard, the technological process involving the several cycles of polishing the dies material by the low energy electron beam irradiation was developed. For this purpose, the following sequence of operations was developed and implemented:

Diaphragm was installed on the electron gun;
Grid was mounted;
Third magnetic field coil was installed under the processed object
Desired diameter of the cathode was chosen;
Cathode configuration was chosen;
Anode diameter was determined;
Scanning by the electron beam was used.

These operations, both jointly and separately, were used to optimize the conditions of electron beam irradiation. As a result of the manufacturing application, the duration of the operational cycle of the products production without shrinkage was reduced.

4. *Medicine:*

Stents. A technique for the myocardial infarction therapy using the stent deployment and fixation in the coronary arteries is widely used. To smooth the burrs on the stent after laser cutting, it is exposed to the acid etching and electron beam processing by 40 shots. The stent is set on a wooden holder which is rotating on an angle of 90° around the axis (tilt angle is 5~10 °).

Nickel-titanium guide wires. The electron beam irradiation of NiTi guide wires can lead to an increase in the corrosion resistance. To increase the fatigue endurance, an additional acid treatment is used. The internal stresses in bending and the cracks size are reduced by means of the annealing. Small cracks and dents can be attributed to the formation of the precipitated phase of Ni_4Ti_3, which is the reason for the reduction of the bending strength. The optimum mechanical properties of NiTi guide wires treated by an electron beam can be obtained by varying the annealing conditions to slow Ni_4Ti_3 phase separation. This can be clearly seen in figure 3.6 after aging at 500° C for 1 hour (see Fig. 3.3).

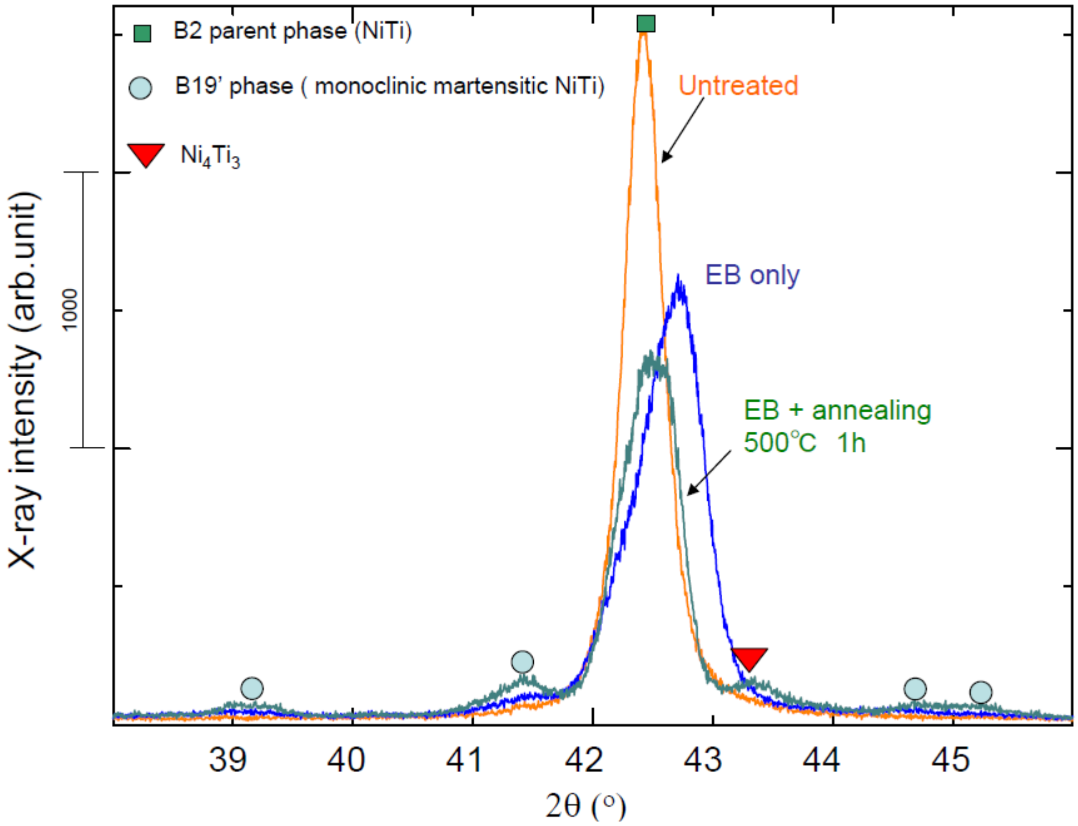


Figure 3.3. Intensity of *Ni_4Ti_3* in NiTi samples after treatment by the electron beam and annealing

Hip bone and knee bone joints. When the joints made of metallic materials are exposed to the electron beam, high corrosion resistance, high bio-compatibility, high hardness and low surface roughness are obtained. These factors increase the wear resistance and lower the friction coefficient.

Artificial tooth and denture. Currently, the artificial tooth and denture are dominantly made with precious metals (e.g., Au-Ag-Pd). To process them by the electron beam is proposed to reduce the surface roughness, enhance brightness and improve the corrosion resistance. The best effect with the least amount of processing cycles is achieved by the additional use of titanium whiskers bed.

Fixations of broken bones. These are made of titanium alloys. On the surface of products processed by the electron beam, thin fine-grained re-crystallized layer modified the core structure is formed. At the same time, the smoothing of the surface is obtained, which positively affects the erosion resistance.

5. *Cutting tools*. Currently, the cutting tools which can work without special cooling are widespread in the industry. In this regard, the hard diamond like carbon coatings with low friction are in high demand. The main task is to increase the coating to the tool surface adhesion. The adhesion properties of the

coating are determined by the oxygen and nitrogen impurities during the deposition. Ion implantation of TiB_2 improves the coatings quality, does not change the dimensions of the tool and double reduces the wear. The contact zone of the tool with the work piece at a depth of 3~5 microns is being heated to the melting point of steel.

6. Engine parts. It is found that when lubricating, the hydrogen-free diamond-like carbon films have lower friction coefficient than the diamond like carbon film containing hydrogen, due to the absorption of Glycerol mono-oleate (GMO) in the lubricant. In this regard, it is necessary to ensure a good adhesion of coatings and a stable friction coefficient, that not increasing with wear.

7. Diamond like carbon films coating on graphite. The silicon ingots are made with CZ process with isotropic graphite crucible and the diamond like carbon coating for the crucible in the semiconductor industry demanded. In this regard, the formation of the diamond like carbon film coatings shows considerable difficulties. We have managed to find a mode of the diamond like carbon film coatings formation with an increased hardness and good adhesion. This is ensured by heating graphite in vacuum at 200° C during 2 hours.

8. *Nano-carbon, nano-carbon bulbs and nano-diamonds.* There are two ways to create them. One of them is production "diamonds from soot" in the dry form, as it is shown in Fig. 3.4.

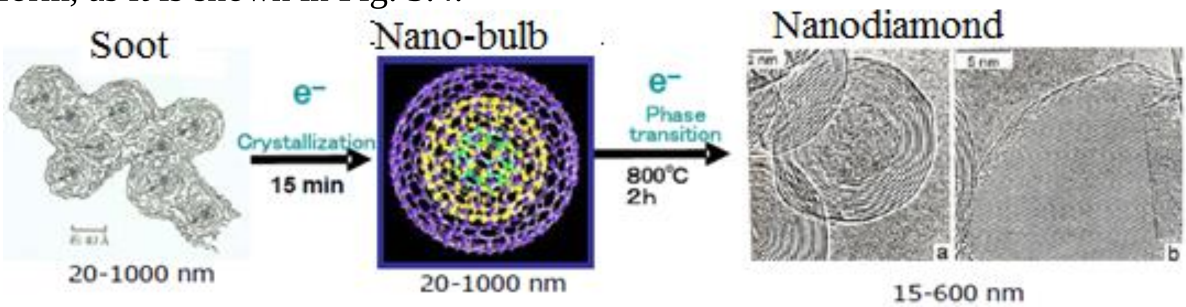


Figure 3.4. The scheme of formation of the nano-diamonds from nano-carbon bulbs

Earlier the nano-bulbs were generated and observed only in the transmission electron microscope (TEM) after a long-term exposure. We have transformed graphite into the graphite nano-onion by means of the electron beam irradiation. Large particles of nano-onions with a diameter of 90 nm could be obtained from the amorphous graphite using the pulsed irradiation (30 kV, 100 shots). In this method, "copper plasma" acts as catalyst for the nano-onions synthesis. Both the electron beam, plasma from the copper and the high density are necessary ingredients in this method. The transition of the isotropic graphite into the nano-onion can be achieved at the current density of 17 kA/cm^2 and the energy density of 78 J/cm^2. According to the analysis performed on TEM, after two years of aging of the sample, the nano-onions exhibit stable (see Fig. 3.5).

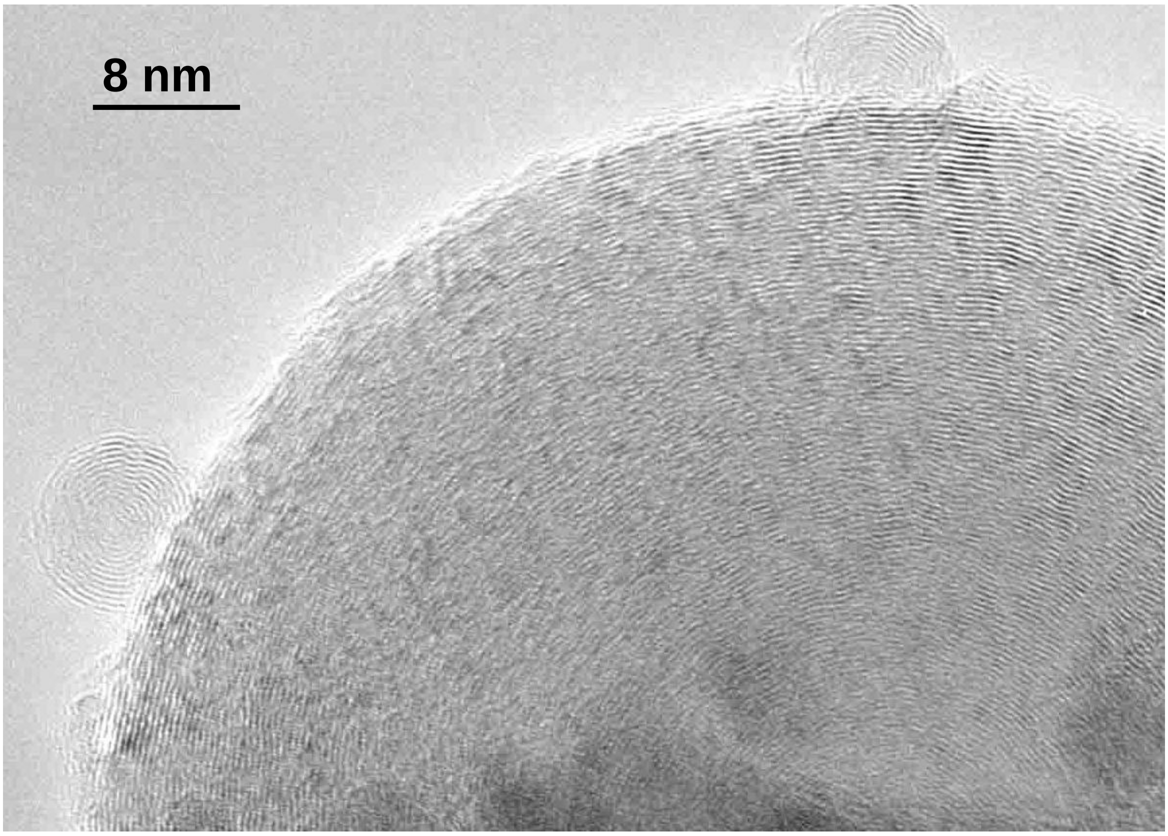


Figure 3.5. The HRTEM of nano-carbon onion

The transformation of the structure occurs due to the destruction of carbon bonds caused by electron beam, carbon atoms liberation and the temperature rise. The temperature reached may be sufficient to vaporize the graphite due to the high current density.

9. *Surface polishing by ultraviolet radiation.* The surface polishing of the polycrystalline diamonds and diamond-like carbon coatings are carried out by ultraviolet radiation together with TiO_2 photo-catalyst. On the surface of the photo-catalyst, the reactions of oxidation and reduction occur (see Fig. 3.6). This method allows removing the CO_2 carbon atoms from the surface. The oxidation is stimulated by TiO_2 photo-catalyst, which provides the generation of the oxygen and hydroxyl radicals using photo-catalysis. The polycrystalline diamond with an initial roughness *Ra* 0.278 µm, *Rz* 1.840 µm after the UV with TiO_2 powder treatment for 2 hours has achieved the following parameters: Ra 0.062 µm and Rz 0.060 µm.

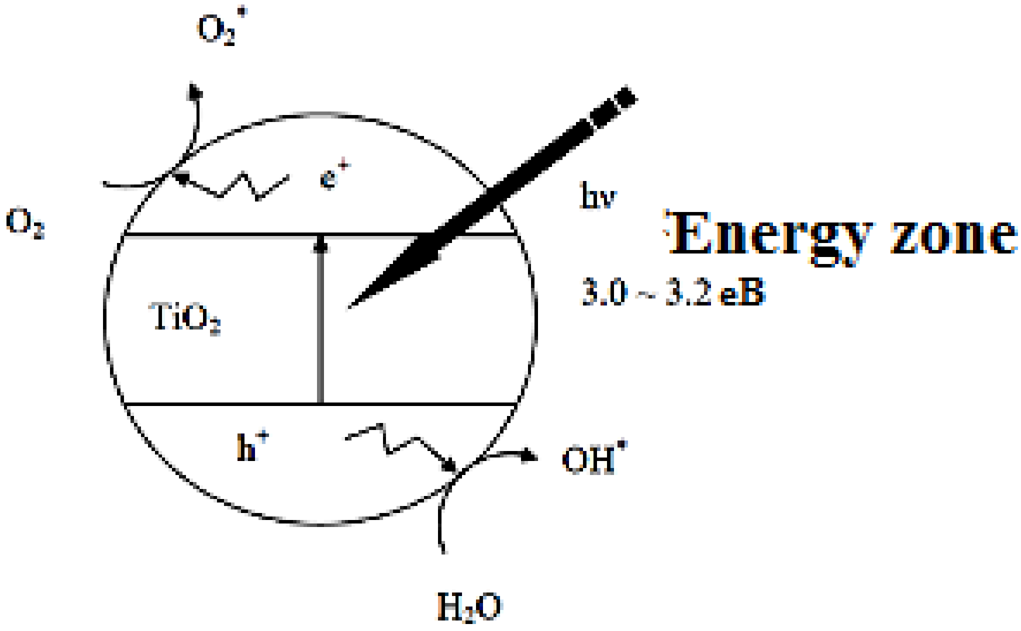


Figure 3.6. The reaction mechanism of photo-catalysis using TiO_2

This mechanism of CO_2 generation, shown in Fig. 3.9. represents two stages:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow OH* + H^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2* \quad (3)$$

$$O_2* + H^+ \rightarrow HO_2* \quad (4)$$

$$C + OH* \rightarrow COH* \quad (5)$$

$$COH* + HO_2* \rightarrow CO_2\uparrow + H_2O \quad (6)$$

Titanium dioxide in combination with nitrogen when adding pure titanium dioxide ($TiO_2/TiO_{2-X}N_y$) has a higher photo-catalytic activity than anatase (see Fig. 3.7).

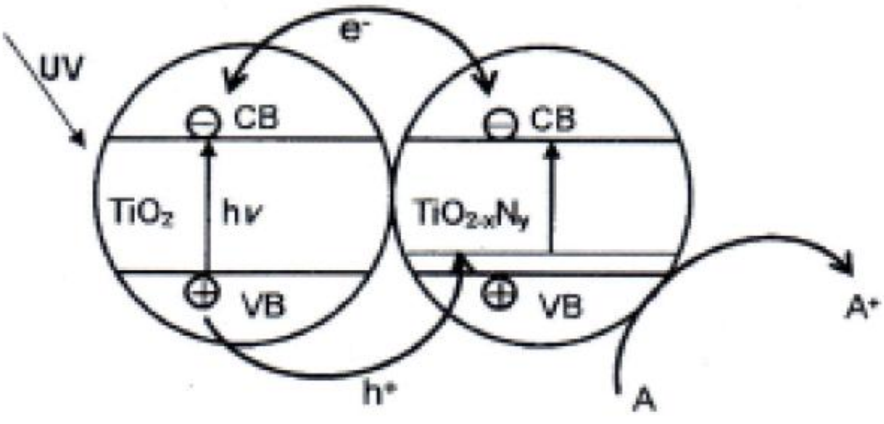


Figure 3.7. The scheme of the photon induced charge separation on the compound of $TiO_2/TiO_{2-X}N_y$

The reaction can be described by the following equations:

$$CH_3CHO + H_2O + 2h^+ \rightarrow CH_3COOH + 2H^+$$
$$CH_3CHO + 3H_2O + 10h^+ \rightarrow 2CO_2 + 10H^+$$
$$CH_3COOH + 2H_2O + 8h^+ \rightarrow 2CO_2 + 8H^+$$

8. *Consumer goods - razor blades.* Sharpening of the blade tip is accomplished by the plasma exposure. In this case, the surface sputtering by the inert gas plasma ions occurs. The main parameter of the power source for this treatment is a uniform current density along the surface of the blade. The most effective ion source for processing of the large surfaces is the accelerators with a closed electron drift and a narrow acceleration zone. The generators of gas plasma based on the gas discharge with a thermionic cathode are used for the high performance processing by the plasma ions with a concentration of up to 10^{10} cm^{-3} at a pressure of 0.8~1.5 Pa.

The nitriding provides the heating of the blades to 350 °C, thus the diffusion of nitrogen atoms on the blade surface begins. The cathode of the arc plasma generator is a combination of a hollow plasma cathode and the thermionic cathode. The parameters to be varied are the density of blades on the holder, the distance from the ion source, the orientation of the blades relative to the axis of the ion beam, the value of accelerating voltage and the ion current. At the voltage of 800 V and the chamber pressure of 1.2 Pa, the bias source provides the desirable regime of the treatment. In this case, the average discharge current was 8~12 A. It made possible to create a blade with a sharpening angle of 16° and a radius of rounding of 300 Å.

Conclusion

The results of the conducted investigations:

- It was shown that ion implantation of *Ar* into the super hard alloys based on tungsten carbide is more effective than N_2 implantation at low doses. The friction coefficient in case of *Ar* use decreases 30% in comparison with N_2.
- It was found that during ion implantation into steel SKD11 the hardness is considerably increased when using N_2. The friction coefficient decreases 3 times and twice in case of *Ar* use.
- As the result of the conducted investigations technological process which includes several cycles of material polishing by low energy electron beam was developed. The works to harden forming dies, extrusion dies, different medical devices (stents, nickel-titanium guide wires, hip and knee bone joints and dental prosthesis, etc.) were carried out.
- The investigations were made and graphite was transformed into graphite nano-onions by means of the high current electron beam irradiation. Large particles of nano-onions with the diameter of 90 nm could be obtained from the amorphous graphite using the pulsed irradiation (30 kV, 100 shots). In this method, "copper plasma" acts as the catalyst for the nano-onions synthesis. The transition of nano-onion into nano-diamond, invented by Bankhart, was

combined with the concept "diamonds from soot" as the second step of crystal improvement.

- The investigations conducted in the field of plasma beam methods of product modifications from metal materials allowed to implement a number of installations in the industry. Special attention was paid to the combined methods of service properties improvement of the products of different applications.

The following fields of practical application can be emphasized:

- polishing and the service properties improvement of the extrusion dies from super hard alloys when using pulse electron beams;
- service properties improvement of the press-forms and the forming dies on the basis of application of pulse electron beams combined with the deposition of diamond like carbon coatings;
- the improvement of corrosion properties and bio-compatibility, surface roughness decrease of a number of products used in medicine, i.g. stents, nickel-titanium guide wires, hip and knee bone joint, fixators of the broken bones, dental prosthesis from precious metals.
- service properties improvement of the shaving blades when using plasma nitriding.

During experimental investigations the laboratory equipment developed in the Institute of High Current Electronics, Siberian Branch of the Russian Academy of Sciences (under the supervision of professor Koval N.N. and professor Proskurovsky D.I.), Tomsk Polytechnic University (under the supervision of associate professor Brukhov V.V.), the Institute of Electrophysics of the Ural Division of the Russian Academy of Sciences (under the supervision of professor Gavrilov N.V.), in the Institute of Metal Physics of the Ural Division of the Russian Academy of Sciences (under the supervision of professor Trakhtenberg I.Sh.) was used.

In this research almost all kinds of connections between properties of thin films and surface modification have been analyzed. A particular attention was paid to the combined effect. The use of such technology is constantly exposed to competition, requiring constant improvement of the already obtained results, especially in the field of medicine. Research will be continued and reported in the future.

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