Project no.: INCO-CT-2005-016805

Project acronym: RTCNANOHARD

Project title: **Strengthening the Research and Technological Capacity in the Field of Nanostructured Thin Films, Hard and Superhard Coatings**

Instrument: Specific Support Action - 2

Thematic Priority: 3

FINAL REPORT

Period covered: from April 2005 to September 2007

Date of preparation: 05.11.2007

Start date of project: 01. 04. 2005

Duration: 30 months

Project coordinator name: Roumen Kakanakov
Project coordinator organisation name:
Institute of Applied Physics,
Bulgarian Academy of Sciences

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Final report

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1. Final activity report

1.1. Project execution

INCO-CT-2005-16805 RTCNANOHARD is a project for Specific Support Action of the Sixth Framework Program, Priority 3: "Nanotechnologies, multifunctional materials and new production processes". It started on 1st April 2005 with a duration of 30 months and financial contribution of the European Commission in an amount of 150 000 Euro.

The goal of the project was reinforcement the scientific potential and technological capacity of the Institute of Applied Physics (IAP) in the field of nanostructured thin films and response the needs of the Bulgarian industry in hard and superhard coatings. In accordance with the scope of the programme Integrating and Strengthening the European Research Area, this goal has been realized by achieving the project objectives:

1. Enhancement of the research potential in the field of nanostructured thin films, hard and superhard coatings.
2. Improvement of the technology capability of deposition and characterization of nanostructured thin films, hard and superhard coatings on various stainless and cutting steel, silicon and silicon carbide substrates.
3. Adapting the technology of hard and superhard coatings for industrial application.

The Institute of Applied Physics with Small Enterprise (SE) was the project coordinator and the only participant. Because of the specific combination of the scientific work, performed at the Institute and development and production doing at the SE, IAP became an unique place for creating new technologies, their adapting to industrial application as well as dissemination of knowledge and related information.

PROJECT MANAGEMENT

The project management was carried out by the Management team, which consisted of the Project Coordinator Dr. Roumen Kakanakov and the Workpackage Leaders Dr. Peter Svestarov, Dr. Lilyana Kolaklieva, Dr. Gencho Sarov and Res.Sci. Tetyana Cholakova. The project team was responsible for the successful fulfilment of the workplan and the project in totally as well as the project administration including dissemination of information and building consensus between the project groups.

Leading specialists from the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences (Sofia), the University of Sofia and the Technical University of Plovdiv were appointed as local experts. Foreign experts from leading European scientific centres in nanostructures, hard and superhard coatings were invited to participate at the project management. The following leading scientists gave their assistance to the project: Prof. Dr. Dr.h.c. Stan Veprek (Technical University of Munich, Germany), Prof. Luis Rebouta (Universidade do Minho, Portugal), Prof. Steve Bull (Newcastle University, UK), Prof. Dr. E. K. Polychroniadis (Aristotle University of Thessaloniki, Greece), Prof. Erik Janzén **(**Linköping University, Sweden), Dr. Volker Cimalla (Technical University Ilmenau, Germany), and Assoc. Prof. Dr. Cevat Sarioglu (Marmara University, Turkey).

The project management is schematically presented in Figure 1.

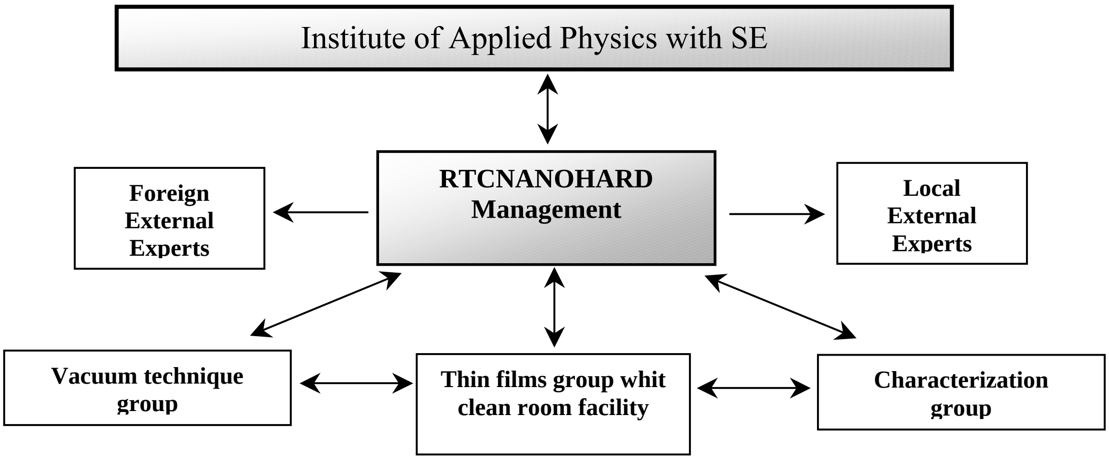


Figure 1. Project Management Structure

The Management Team activities included detailed work coordination, fulfilment, monitoring and reporting the Workpackages. The Management team realized them using the following tools:

- <u>Regular Workpackage group meetings according to the specific needs of the task</u>

Weekly Workpackage group meetings were held. The progress of the Workpackage tasks (on-going or completed) was reported, the arisen problems were discussed and solved and the work for the next period was defined at them. Minutes of each meeting had been taken for further reference.

- <u>Supervision of the Vacuum technique group and Design team</u>

By reason of great importance of the PVD equipment renewal and upgrade, a Design team was established in the Vacuum technique group. Its work was focused on design, building and testing the new equipment parts such as cathodes of a new generation, new contactless arc igniters, new massflow controllers and etc. This team was responsible for the completely equipment automation including both: equipment and technology control.

- <u>Supervision of the team for building new electro-discharge polishing equipment</u>

The electro-discharge polishing is a technology attendant the PVD technique. It is developed by the specialists at IAP. The success of electro-discharge polishing during the first stage of the project had attracted the attention of many external customers and was the incentive to start building a second unit designed for industrial application. New modernised 30 kW EDP equipment was built. It enables the pre-PVD plasma polishing of larger parts (sized about 600 cm^2).

- Regular workmeetings with local experts and IAP workpackage leaders

Regular work meetings with local experts Assist. Prof. Dr. Sv. Evtimova from the University of Sofia and Assist. Prof. Dr. A. Zjumbilev from the Technical University of Plovdiv and IAP workpackage leaders were held during the whole reporting period. These were dedicated to characterisation of hard coating films developed at IAP and interpretation of the measurement results.

International workmeetings

- International workmeeting with Prof. Dr. Polychroniadis from the Aristotle University of Thessaloniki was held on 1st June 2006 in Plovdiv. Issues related to the composition and morphology of TiN on SS420 substrates produced on our PVD equipment were discussed. The results of structural studies by Scanning Electron Microscopy and Transmission Electron Microscopy performed at Prof. Polychroniadis' laboratory were reviewed. Possibilities to improve the coating morphology were delineated.
- The workmeeting with Prof. Dr. Polychroniadis was held on 14th of May 2007 in Velingrad during the Workshop NANOHARD 2007. The outline of workmeeting included discussion on investigation by TEM and SEM of ZrN coatings obtained at IAP and planning the further collaboration in nanostructured thin films and superhard coatings.
- A work meeting with Prof. Bull and IAP senior scientists took place during the Workshop NANOHARD 2007 in Velingrad on 15th May 2007. Reliability of micro- and nanoindentation hardness data was discussed. Agreement was reached coated specimens produced at IAP to be characterised by nano- and microindentation at Prof. Bull's laboratory at the University of Newcastle as a comparison with measurements done in Bulgaria.

Business workmeetings

During a two-month period, in February and March 2007, several business workmeetings were held with our end-user FESTO Ltd.

The companies showed an interest in coating hard-alloyed steel tools and specialized moulds aimed at increasing the wear resistance. Their demands regarding microhardness, adhesion, wear resistance; coating type and thickness were specified.

- Control of caring out the orders of clients

After popularisation of the work and results of the project (through advertising, Internet pages, etc.) and especially after the International conference, IAP has received orders from different companies regarding:

- Deposition of different coatings of (Ti, Al, Cr, Zr) nitrides and carbides or their combination. Orders from companies Remi Ltd., FESTO Ltd., AREXIM Ltd. have been received
- Polishing stainless steel tools using electro-discharge polishing technique. Companies LaserArt Ltd. and Comeco Ltd. became our permanent clients.
- Purchase equipment and technology for coating deposition.
- Purchase equipment and technology for electro-discharge polishing. Companies Comeco Ltd. and Titanit Ltd. ordered 30 kW EDP equipment and relevant technology know-how.

- Financial control of the project

The Management team realized permanent control on ordering and purchase of the parts necessary for the upgrade and automation of the PVD equipment. It also required from the project accountant annual financial reports about the project finances once in three months.

- Control on the fulfilment of the project deliverables

The project had totally 16 deliverables. The Management team followed very carefully on time and quality fulfilment of the deliverables as well as solved the problems arose regarding the achievement. A reminder was given to the person responsible for the deliverable when the deadline was coming close. The necessary documentation for the deliverable also was subjected to referring and approval.

- Project monitoring

The project progress was verified by Monitoring, so timely actions could be taken when necessary. Two critical indicators, time and quality, were controlled. The Management Team supervises three working groups from the Institute of Applied Physics with SE. Continuous Control was practiced day-to-day and during the implementation of Project Workpackages. The authority to implement this control was granted to the Management Team and in crucial cases to external experts as follows:

- Within an each workpackage team meetings were organized usually once weekly. At them current problems were delineated and progress reported.
- Detailed co-ordination of Workpackage groups was being performed currently once weekly at work meetings. Progress in each workpackage and its tasks was being reported and appearing problems were assigned corresponding priorities to have them completed on time.
- The project Coordinator together with the Management Team duly controlled the timely and quality completion of the project deliverables.
- The management team considered the innovations as a third priority together with the education and research. The innovating culture and innovative actions were the main driving force for positive change. This was the tool that would provide the successful implementation of project activities. This responded to the need to promote and adopt innovative culture in research and education as well as new organizational models suited to present day needs.

- Cultivating innovative culture within the project members

Young members of the project team were taught to regularly read and follow new publications in the field of hard materials, thin film technology, measurement and characterization techniques and etc. Senior members had acquired skills to work in dynamically founded teams dedicated to efficient and on-time accomplishing varied tasks related to supervision, technology and on-going education and learning. Communication between the academic research and the industrial sector had been enhanced through regular business meetings and presentation of our application-oriented projects and accomplishments.

- Organizing preparation and submission reports required by European Commission

The expert meetings were summoned by the project coordinator after the reporting period expiry and before the reporting deadline. During the report writing they were held daily and approve the relevant workpackages and financial reports. The annual and final reports were discussed at them.

The work on the project was organized in five Workpackages, whose objectives and tasks corresponded to the project goal and objectives, respectively. Achievement of the workpackage deliverables was a criterion for the successful workpackage fulfilment. The workpackage organization and relation between them are presented in Fig. 2.

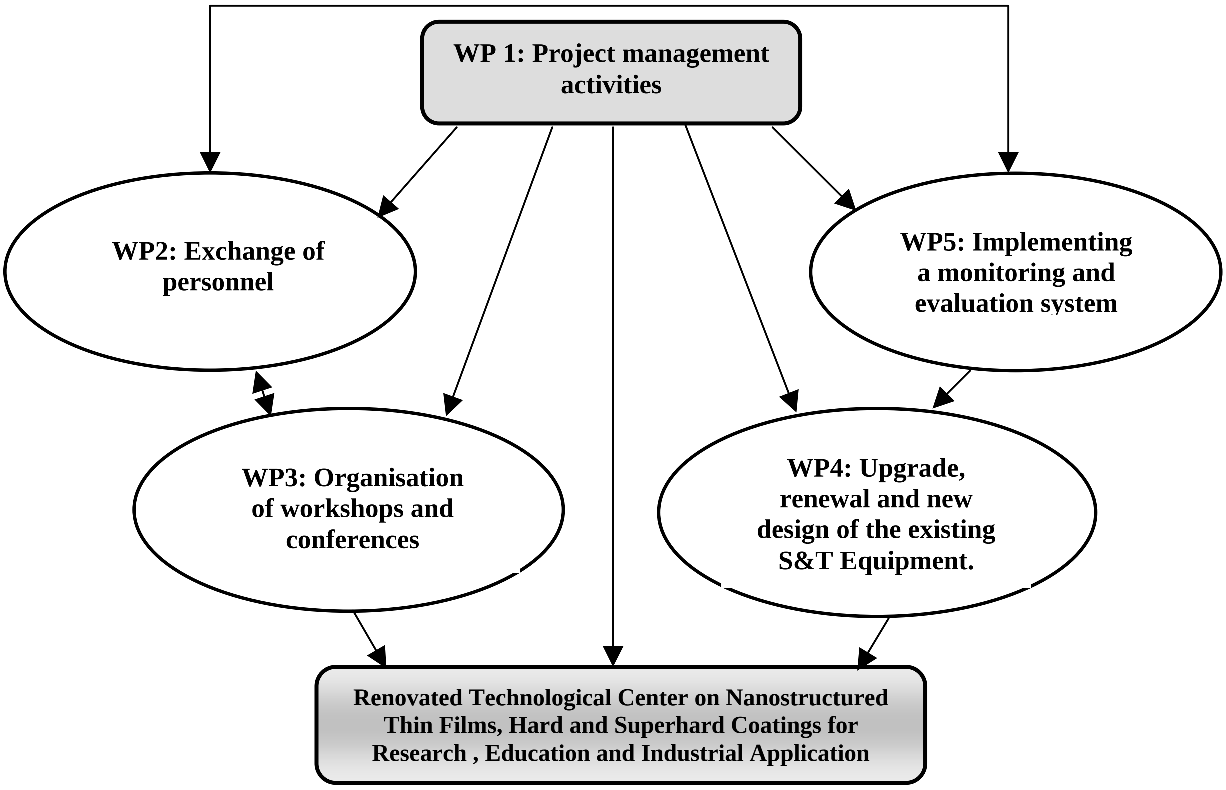


Fig. 2. Work organization of the project RTCNANOHARD

The activities of the IAP team on each workpackage were focused toward the achievement of the project objectives and will be summarized in accordance with them.

<u>PROJECT OBJECTIVES FULFILMENT</u>

1. **<u>Enhancement of the research potential in the field of nanostructured thin films, hard and superhard coatings.</u>**

In summary, this objective has been fulfilled by the following activities:

- Organisation of activities with regional, national and international impact such as an international conference, workshops and work meetings, at which leading scientists will be invited to participate and to give plenary talks.
- Organisation of lecture cycles at IAP based on the visit of leading researchers from the Linöping University, the Aristotle University of Thessaloniki, the Technical University of Munich, the University of Guimaraesh and the Marmara University in Istanbul.
- Teaching of Master students, Ph.D students and post-doc students in order to reinforce the young research potential creating specialists suited to applied research and further self-improvement.

In the frameworks of the project three scientific forums with national, regional, and international impact were organized and performed for knowledge dissemination and enhancement of the research potential in the field of nanostructured thin films, hard and superhard coatings:

- International Workshop NANOHARD 2005 "Nanostructured thin films – technological base of a new generation of microelectronics devices and superhard coatings", 19 –21 October, 2005 in Plovdiv.
- International Conference NANOHARD 2006 "New trends in development of nanostructured thin films, hard and superhard coatings", 28 – 31 May, 2006 in Sozopol.
- International Workshop NANOHARD 2007 "Development, characterization and industrial application of nanostructured thin films, hard and superhard coatings", 13 –16 May, 2007 in Velingrad.

These events were organized and hosted by the Institute of Applied Physics. They were widely notified by created a web site (www.nanohardbg.com until 30 September 2007, www.nanohardbg.com after that) as well as personal contacts by e-mails using address base created. The information about the forums was disseminate among the Bulgarian scientific community also by placards placed in all scientific institutes and high schools, which have activities corresponding to the forum theme. The conference and workshops topics corresponded to the forum title and covered nanocomposite films, hard and superhard coatings, technologies and equipment for deposition of nanocoatings, nanomaterials and thin films for solid state electronics and energy technologies, processing of nanostructured thin films for solid state electronics and energy technologies, thin films characterization, control of structure and properties of nanomaterials. A special attention was given to industrial application of hard and superhard coatings.

The forms were attended by 33-37 scientists, engineers and specialists from 8 countries totally of Europe, Asia and Australia, among them United Kingdom, Germany, Portugal, Sweden, Greece, Switzerland, Belgium, Turkey, Belarus, Russia, Republic of Macedonia and Bulgaria. Researchers from 7 Scientific Institutes at the Bulgarian Academy of Sciences and 7 Universities were participated as well. The workshops and conference were also attended by specialists from industrial companies working in this field: CSM Instruments SA (Switzerland), Surftech Pty.Ltd. (Australia), Titanit (Turkey), Plasma Ltd. (Republic of Macedonia), FESTO (Bulgaria), AREXIM (Bulgaria) and Milko Angelov Consult (Bulgaria).

The conference and workshops were organized in plenary and poster sessions. Invited talks were given by European scientists who are leaders in the field of thin films, hard and superhard coatings: Prof. Dr. Dr.h.c. Stan Veprek (Technical University of Munich, Germany), Prof. Steve Bull (Newcastle University, UK), Prof. Luis Rebouta (Universidade do Minho, Portugal), Prof. Erik Janzen (Linkoping University, Sweden), Prof. Dr. E. K. Polychroniadis (Aristotle University of Thessaloniki, Greece), and Assoc. Prof. Dr. Cevat Sarioglu (Marmara University, Turkey), Dr. Volker Cimalla (Technical University Ilmenau, Germany). These leading scientists shared their knowledge, experience and recent results on development, properties and methods for characterisation of nanostructured films and new materials.

The presentations at the forums NANOHARD were reviewed, edited and published in Proceedings of each event. Each book of proceedings had a printing of fifty with own ISBN code. The proceedings were disseminated between the participants as well as other scientists interested in nanostructured thin films, hard and superhard coatings. For more flexible dissemination of the presentations a CDs with proceedings were created as well.

The success of the International Conference and Workshops NANOHARD was due to the high scientific level of the lectures and informal atmosphere of the followed discussions during the plenary and poster sessions ensured by the session chairpersons. NANOHARDs became forums at which not only the results from development and scientific study of nanostructured thin films, hard and superhard coatings were presented but also the problems of their industrial application were discussed. Thereby the forums NANOHARD really realized dissemination of the knowledge in the field of nanostructured thin films, hard and superhard coatings and contributed to the enhancement the research potential at IAP and in the region. They created new scientific relations between the Bulgarian scientists and the scientists of leading European groups and opportunities for further joint research and developments.

Visits of leading European researchers in Bulgaria were organized for the benefit of the national research community and IAP staff in the field of hard and superhard coatings and thin film science. The visits usually took a place during the scientific forums organized in the frameworks of the project RTCNANOHARD: NANOHARD 2005, NANOHARD 2006 and NANOHARD 2007. The guest professors delivered invited state-of-the art lectures in the field of thin films and materials science highlighting key aspects of hard and superhard coatings. Besides the lectures the leading experts discussed and consulted with IAP research staff the equipment design, upgrading and automation. Possibilities for hardness measurements and structural studies at European research centres were discussed; the needed arrangements were made, scheduled and effected in force.

Besides the lectures delivered by Prof. St. Veprek, Prof. E. Janzen and Prof. E. Polychroniadis at the IAP scientists, additional lectures on nanostructured materials and thin films were organized. They were delivered by guest visitors form other research laboratories working in the same field: Prof. D. Domanevskii, Dr. Y. Trofimov, V.D. Jitkovski. The colleagues Acad. A. Petrov and Assoc. Prof. Dr. E. Vlahov from the Institute of Solid State Physics of the Bulgarian Academy Sciences presented their last results on investigation of nanostructured matetials. Possibilities for joint work were also discussed at these visits.

The regular workmeetings with Assoc. Prof. E. Trifonova and Assoc. Prof. S. Evtimova from the University of Sofia, Assoc. Prof. A. Zjumbilev from the Technical University of Plovdiv, Prof. Ts. Marinova from the Institute of General and Inorganic Chemistry of BAS were held for the purpose of characterisation of our coated samples. At these meetings the measurement techniques and obtained results were discussed because of that they also contributed to the enhancement of the research potential at IAP.

The efforts of the project team were directed also to reinforce the young research potential creating specialists suited to applied research and further self-improvement by teaching Master students, Ph.D students and post-doctoral students.

The young physicist with a Master degree in solid-state electronics Emil Pashkulov had been trained to operate the PVD equipment. After that he operates and services it on regular basis. His responsibilities cover vacuum coating process performance and routine mechanical, electrical and electronic maintenance tasks.

The young bachelor of electronics Maria Enevska was employed at IAP. She started Master study at the Technical University of Plovdiv and prepared Master Thesises. IAP and this project provided her the environment and conditions for work on Master Thesises. The Thesises theme directly related to the tasks for equipment upgrade and development of hard coating technology.

By the last period of the project two new doctorants Nikolay Petkov and Vassiliy Chitanov have been employed at IAP. The thematic of their dissertations correlate very closely with the tasks for completely computerizing and automation of the PVD equipment and technological process:

Nikolay Petkov, was a doctorant at the Technical University of Plovdiv for the period 2004 - 2007 under the direction of Assoc. Prof. Dr. Ivan Ganchev. The theme of his dissertation is “Autotuning of Controllers and Diagnostic”. During his Ph.D. study he specialised at the

Institute of Automation and Control at the Technical University of Graz, Austria (9 months) on Ern Macht Stipendium (ÖAD Stipendiant) and at the Technical University of Prague (3 months) on the EC program Erasmus.

Vassiliy Chitanov, was an external Ph. D. student at the Technical University of Plovdiv for the period 2004 - 2007 under the direction of Assoc. Prof. Michail Petrov. The theme of his dissertation is "Model Predictive Control of Polymer Processes". He specialised at two departments of the Aristotle University: the Laboratory for Polymer Reaction Engineering (LPRE) for 1.5 year by the support of the European program BatchPro and the Chemical department for polymer engineering for one year on the EC program Erasmus. He also specialised at the Technical University of Prague for four months and was supported by the Central European Program CEEPUS.

Both doctorants have entered the completion phase of their Ph. D. studies and a dissertation defences is forthcoming. The IAP will support the defences of their dissertations.

By achieving this objective the research potential at IAP has been enhanced; knowledge in the field of nanostructured thin films, hard and superhard coating was disseminated between the scientific community in Bulgaria and the region; new scientific relations between the Bulgarian scientists and the scientists of leading European groups have been created, which gives opportunities for further joint research and developments; and the young research potential has been reinforced and specialists suited to applied research and further self-improvement have been created.

2. Improvement of the technology capability of deposition and characterisation of nanostructered thin films, hard and superhard coatings on various stainless and cutting steel, silicon and silicon carbide substrates.

The improvement of the technology capability of deposition of nanostructured thin films, hard and superhard coatings has been achieved by activities related to upgrading the equipment available at IAP and realization of feed-back between characterization and technology of the coatings.

After the equipment renewal and upgrade, the work of the team was focused on obtaining the reproducible technological regimes for deposition of nitrides and carbides of transition metals and their combinations being of interest for the industry. The experiments were performed predominantly by the specialists at IAP, as some of them by the assistance of the guest researchers from collaborated groups.

The coatings have been obtained by Cathodic Arc Deposition (CAD) technique as a PVD variant outperforming the other techniques by its higher degree of ionisation, the coating density and adhesion and the overall process efficiency, a crucial issue in industrial applications. However, the presence of macroparticles in the layers deposited by this method deteriorates their quality. Therefore, significant efforts were applied to solve this problem. To improve the coating morphology by decrease of the macroparticle size and quantity and increase the process productivity, two new arc evaporators with controlled magnetic field (CMF) have been mounted into the CAD machine available at the Institute of Applied Physics in addition to the existed permanent magnetic field (PMF) evaporators.

Technology for deposition of TiN, ZrN and CrN single-layered coatings has been developed. These coatings have passed the R&D stages and they are ready for industrial applications. Various binary and ternary metallic coatings such as TiAlN, TiCN, ZrNC, TiZrN have been obtained and investigated also. Both single-layered and compounds were deposited on different types of substrates, namely stainless steel, high-speed steel, tool steel and silicon. Some of developed coatings are presented in Fig. 3.

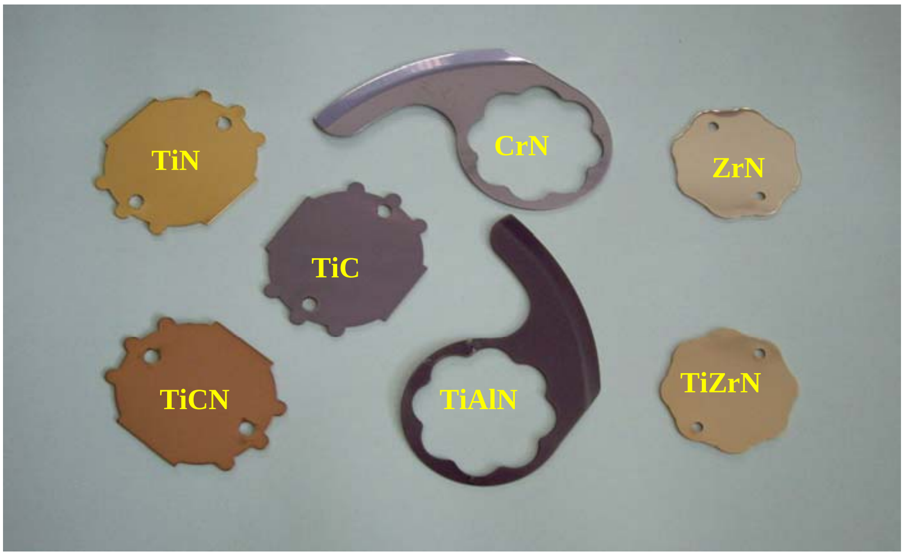


Fig. 3. Tools with different developed coatings

Special attention was paid on obtaining the optimal technological regime for each developed coating and its reproducibility. Therefore several sets of experiments for deposition of Ti, Cr and Zr nitrides and carbides as well as their combination ((TiAl)N, TiCN, ZrNC, TiZrN) were performed at different technological regimes. Strong dependence of coating properties on the physical characteristics of the vacuum arc and induced plasma, which is determined significantly by the design of the vacuum arc deposition system, has been obtained. Different coatings such as TiN, TiNC, AlTiN, ZrN, ZrNC, deposited by Permanent Magnetic Field and Controlled magnetic Field evaporators have been characterized and compared. The technology conditions as vacuum pressure, gas ratio, deposition temperature, deposition time, cathode current, affect on the coating properties as well. This dependence has been observed for all developed coatings and it is illustrated by several ones (TiN, TiNC and ZrN) in a Table 1.

Table 1: Dependence of the coating characteristics on the technological regime.

Exp. No.	P [mbar]	V_D [nm/min]	D [μm]	t_D [min]	H [GPa]
E-TiN / 4	1.5×10^{-3}	40	1. 2	30	13
E-TiN / 14	1.5×10^{-3}	40	3.5	90	24
E-TiCN / 2	2.7×10^{-3} (N_2:CH_4 = 5:1)	42	2.5	60	24
E-TiCN / 3	3.8×10^{-3} (N_2:CH_4 = 5:2)	42	2,5	60	30
E- ZrN / 5	4.5×10^{-3} (N_2:Ar = 30:1)	58	3.5	60	29.5
E- ZrN / 6	2.5×10^{-3}	58	3.5	60	26
E-ZrCN / 1	3.5×10^{-3} (N_2:CH_4 = 2:1)	58	3.5	60	32

The characterization was performed in accordance with the project physical indicators by controlling the following main coating characteristics: thickness, hardness, adhesion, surface morphology.

Thickness

The coating thickness was determined using a Leitz Incident-Light Microscope Interferometer with accuracy of 90 nm. Control measurements were made with a tip profilemeter in order to precise the measurement. The found deviations between both type measurements were in the measurement accuracy. Control specimens with coatings of nitrides, carbides and carbonitrides for thickness measurement were prepared in the same technological cycle together with the coatings deposited on stainless steel and intended for other characterizations. The thicknesses varied in the range 0.5 ÷ 5 μm depending on the deposition time and were found to be with very good reproducibility. The measurements of a number of films showed stable linear dependence of the coating thickness on the deposition time at full control over the other parameters of the deposition process. The deposition ratio was also calculated (see the table). It depends strongly on the cathode material and cathode current, while it does not affected by the vacuum pressure and gas ratio.

Hardness

The coatings hardness was determined using a Vickers hardness tester with a load ranging from 20 to 200g. The coating image was observed on a Leitz microscope. The hardness of the coatings deposited on stainless steel substrates (H=4 GPa) varies in the range 13÷37 GPa depending on the chemical composition of the coatings, i.e. the ratio of the reactive gases, and the film thickness. At small film thickness the influence of the substrate is significant and the determined hardness is lower, respectively. The coating thickness increase leads to increase the measured hardness, i.e. the effect of the substrate decreases and at very thick films could be eliminated. Hence the usual thickness of coatings for industrial applications should not be lower than 2.0 ÷ 2.5 μm. As a result of improved technological capability hardness of 24 GPa (d=3.5 μm), 30 GPa (d=2.5 μm), 30 GPa (d=3.5 μm) and 32 GPa (d=3.5 μm) has been obtained for TiN, TiCN, ZrN and ZrCN, respectively. One of our TiN samples were measured by Professor Steve Bull from Newcastle University, UK. The results obtained from him are: the hardness and elastic modulus is 37 GPa/380, respectively. The load range is from 0.6mN to 10 mN, contact depth from 10 to 94 nm and the hardness is constant over this range. By the standards of hard coating practice this hardness is sufficiently high and Young's Modulus is comparable to such commercial coatings.

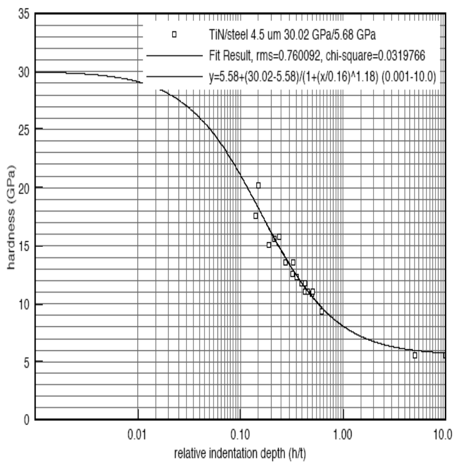


Fig. 4. Composite hardness of TiN coating 4.5 μm thick deposited on stainless steel SS 420.

Methodology for composite hardness determination in the coating depth was developed and applied. It is illustrated on Fig. 4 in the case of TiN coating with thickness of 4.5 μm deposited on stainless steel SS 420 (H=4 GPa).

Adhesion

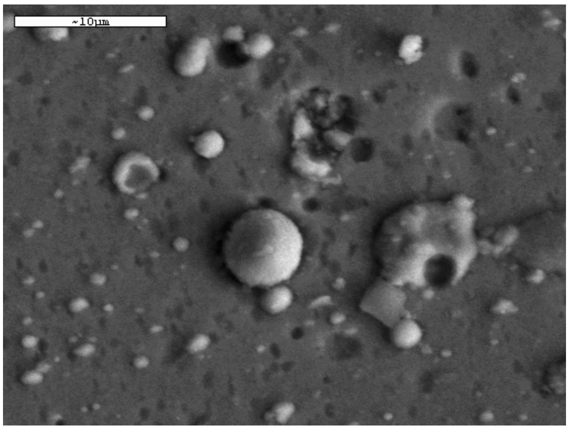
The adhesion measurements were carried out using a scratch tester with 02 mm Rockwell diamond tip indenter at load continuously increased from 0 N to 90 N and scratching speed of 10 mm/min. The critical load was determined from the scratch under optical microscopy observation. For instance, for 3.0 µm thick TiN and TiCN coatings deposited on polished stainless steel substrates critical loads of about 60 N were measured.

The experiments carried out showed that the coating adhesion depends on the film properties (thickness, microhardness) as well as the substrate characteristics (material, surface quality, hardness).

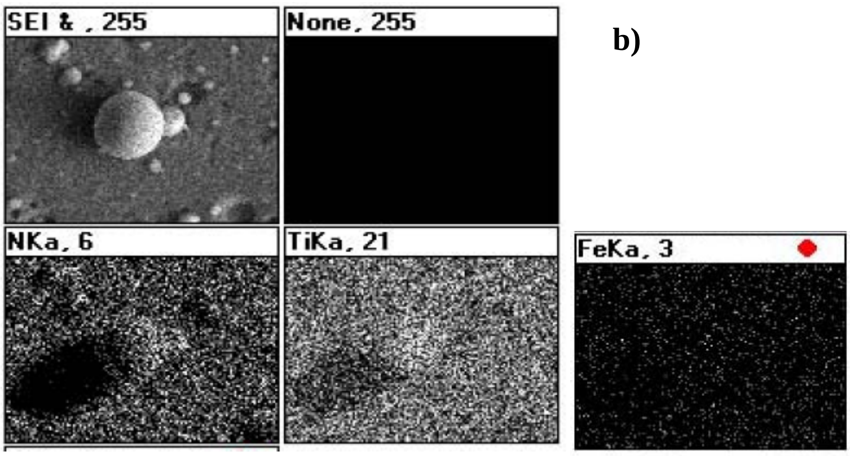
Surface morphology and coating composition

Surface morphology and composition have been examined using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy. The SEM, TEM and AFM analyses were performed at the Aristotle University by assistance of researchers from IAP, while XPS analyses were carried out in collaboration with colleagues at the Institute of General and Inorganic Chemistry.

Specimens prepared in the same technological cycle have been subjected to SEM, AFM and after that to XPS studies. From the same specimens special samples were prepared for TEM investigation. SEM observations revealed that the surface of TiN coatings is rather smooth but not homogeneous because numerous macroparticles and craters spread all over the coatings surface (Fig. 5). However, the macroparticles are reduced and the crater size is also reduced as the N_2 flow increases.



a)



b)

Fig. 5. SEM images from the surface of the TiN coating:
a) 2D image;
b) element contamination.

The surface morphology was observed by AFM. The AFM measurements were performed in contact mode as the images were taken and analyzed from (6.4x6.4) µm² scans. AFM images confirmed the presence of macroparticles and craters observed by SEM (Fig. 6). The surface is

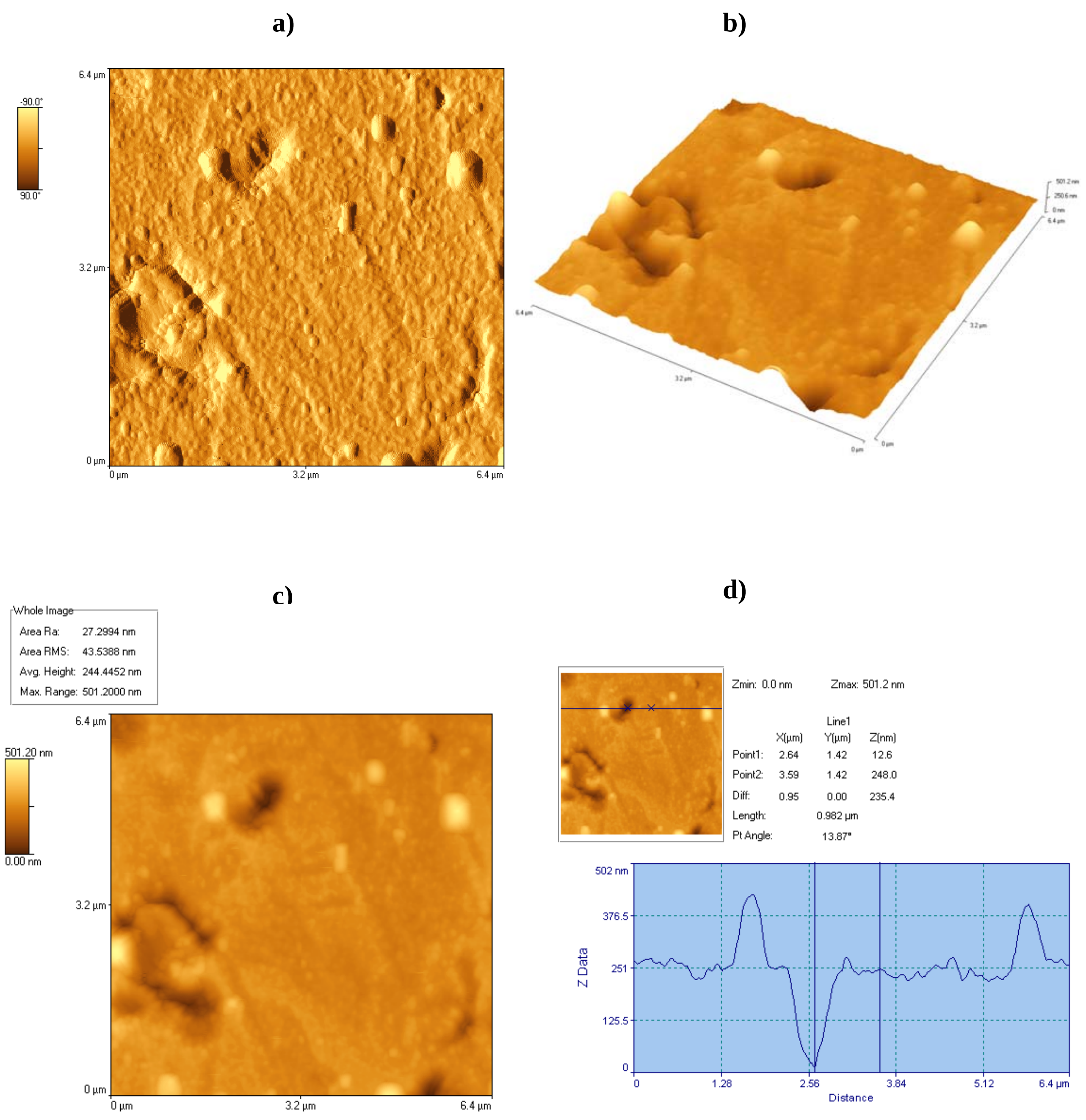


Fig. 6 AFM images from a TiN surface of (6.4 x 6.4) µm^2 :
a) 2D image (z-scale 501.2 µm); b) 3D image of the same surface;
c) average RMS (over whole area); d) RMS between two typical points of the surface.

relatively smooth with average roughness (RMS) of 43.54 nm. However, on areas with macroparticles it increased dramatically. Therefore, the efforts were focused on decreasing the size and quantity of the macroparticles. The surface morphology has been improved by mounting the CFM evaporators. Figs. 7 and 8 compare the surface morphology of coatings deposited by PMF and CMF evaporators, respectively. The surface morphology was observed by a digital Motic MC Camera type 2000 with 2.0-megapixel resolution and the pictures are made at same magnification. The surface of the coating obtained by PMF evaporators (Fig. 7) is rougher with higher quantity of macroparticles. Whereas, the coatings obtained by CMF evaporators (Fig. 8) have almost smooth surface and the macroparticles quantity is smaller on the same size area. Besides, macroparticles resulted from the CMF evaporation are smaller in size and their dimensions do not differ significantly. The most widespread macroparticles have sizes lower than 90 μm, while the biggest size obtained with these coatings does not exceed 131 μm and such macroparticles are rarely on the coating surface. These dimensions are two times lower than the macroparticle size of 263 μm determined for the PMF evaporated coatings. The size of the predominant macroparticles observed on the coatings deposited by PMF evaporators is bigger as well (~106 μm).

From TEM examination it was deduced that the coatings are composed of grains of different

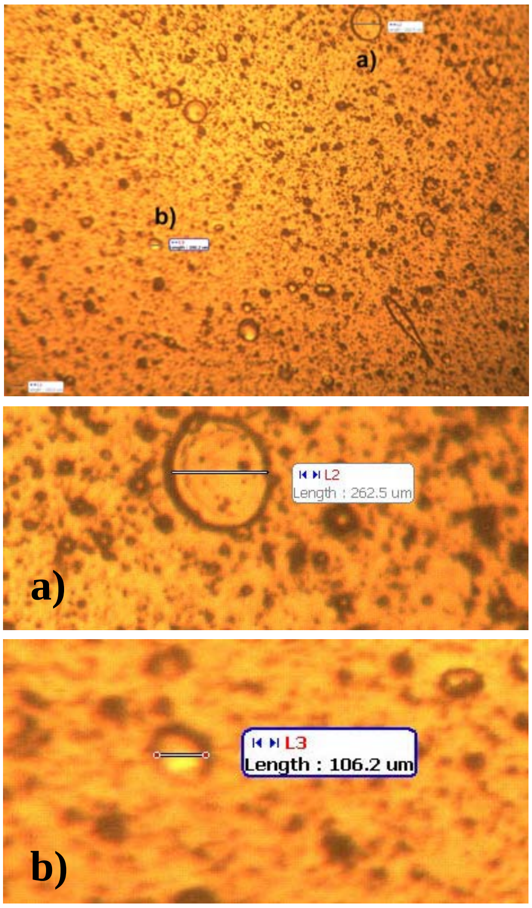


Fig. 7. Surface morphology of TiN coatings deposited by PMF evaporators; a) macroparticles with biggest sizes of 162.5 μm; b) average statistical macroparticles with sizes lower than 106.2 μm.

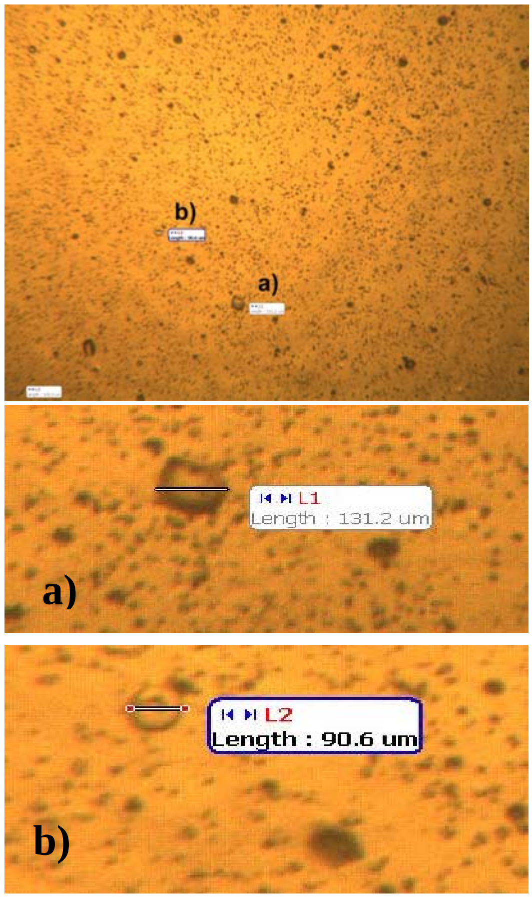


Fig. 8. Surface morphology of TiN coatings deposited by CMF evaporators; a) macroparticles with biggest sizes of 131.2 μm; b) average statistical macroparticles with sizes lower than 90.6 μm.

sizes, grown by the columnar growth mode. The XPS analyses showed that the interface coating / substrate is not abrupt. The presence of Ti an N has been registered even at relatively high concentrations of Fe. The coating stoichiometry depends strongly on the reagent gas ratio.

Special attention was paid on improvement of the preliminary surface cleaning in order to make better the coating quality. The coatings quality depends significantly on the preliminary preparation of the tool surface. Therefore technology and corresponded equipment for electro-discharge polishing (EDP) were developed. These technology and equipment are unique for Bulgaria. Its application before the CAD process allows combining all substrate preparations into a single process that makes the method irreplaceable. The EDP process has main advantages over the standard chemical polishing. EDP removes all surface contaminations resulted after mechanical polishing and allows obtaining the surface roughness RMS ≤ 0.02 μm. Besides, the process is ecological because ecologically clean solutions are used. Application the EDP process for preliminary tool cleaning improved essentially the surface feature and the coating quality, respectively.

In details results from improvement of the technology capability and coating properties are presented in articles published in the Proceedings of NANOHARD 2005, NANOHARD 2006 and NANOHARD 2007.

As a result of the achievement of this objective, reproducible technology for cathodic arc deposition of nitrides and carbides of the metals Ti, Al, Zr, Cr, and their combination ((TiAl)N, TiCN, ZrNC, TiZrN) is available at IAP. Methodologies for characterization of coating properties such as thickness, hardness, adhesion, surface morphology and composition are took possession by the researchers.

3. <u>Adapting the technology of hard and superhard coatings for industrial application.</u>

For adapting the technology of hard and superhard coatings for industrial applications, the available at IAP basic vacuum system was upgraded. The upgrading extends the functionality and capacity of this system converting it into Physical Vapour Deposition (PVD) equipment specialised for obtaining hard and superhard coatings by cathodic arc deposition (CAD)

Fig. 9. Photography of the PVD equipment adapted for R&D and semi-industrial applications.

technique. Photography of the upgraded and automated PVD system is presented in Fig. 9. The renovated system was equipped by a two-wall water cooled vacuum chamber with capacity of 500 litres, two couples cathodic arc evaporators, placed symmetrically on the chamber walls, on which the targets are embed, massflow controllers and all necessary power supplies. Inside the vacuum chamber a multifunctional tool planetary holder and two resistant heaters were mounted. The first couple cathodes are standard equipped with one stabilising electromagnetic coil creating permanent magnetic field (PMF evaporators), while the second couple arc cathodes are original of design. They have two electromagnetic coils, stabilising and focusing, which allows the control of the deposition process by magnetic field (controlled magnetic field (CMF) evaporators). The design of both type evaporators is presented in Figs. 10 and 11. The used three massflow controllers HFC – 302 (0 ÷ 500 sccm) provide precise dosage of the inert (argon) and reactive (nitrogen and methane) gases. Applying a high voltage before the coating deposition the instruments are preliminarily cleaned by ion bombardment. They are also heated to the necessary temperature, which is maintained constant during the deposition process. Because of the Siemens controller and the appropriate software the process of coating deposition was fully automated and computerising. This allows receiving coatings of nitrides, carbides and carbo-nitrides with settled parameters.

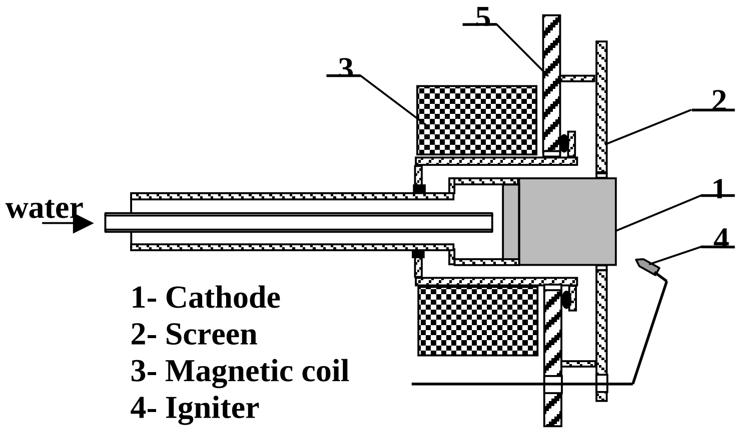


Fig. 10. Principal scheme of an evaporator with permanent magnetic field.

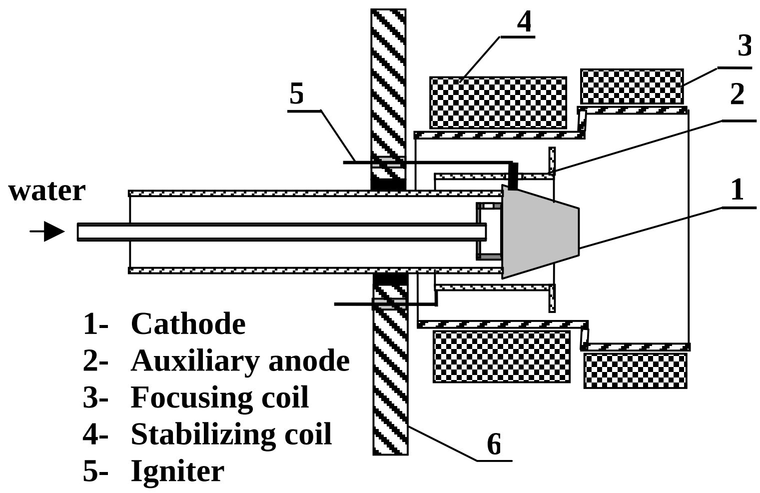


Fig. 11. Principal scheme of an evaporator with controlled magnetic field.

The increased cathode number in the chamber leaded to increase of the deposition ratio and the functionality and capacity of the equipment were enlarged, respectively. As a result a semi-industrial machine was made, that allows to use it not only for scientific R&D and also for fulfilment of the large volume customer orders. The upgrade and automation of the PVD equipment affect on the coating quality and reproducibility as well.

The serious advance in adapting the PVD technology to industrial applications was development of variety of nitride and carbide coatings such as TiN, TiAlN, TiC, TiNC, CrN, ZrN, and TiZrN. As a result of the improved technology capability of deposition a list of recipes was made which will allow facile transfer of different coating technologies to the industry. Fig. 12 illustrates industrial tools covered with different coatings.

Development of deposition technologies for these coatings enlarges our possibilities to respond the needs of the market over the coating assortment besides the increased productivity. The developed technology for deposition of TiN coatings, for instance, was adapted for industrial application and orders of customers Remi Ltd., AFS Ltd., AREXIM Ltd. and FESTO Ltd. have been completed.

Additionally a specialised system for magnetron spattering was put in operation. It will be used for obtaining nanostructured thin films for special purposes.

This way IAP will response to the needs of the Bulgarian and regional markets in hard and superhard coatings, which now are estimated at about to 300 000 tools annually and according to our forecast will grow.

Fig. 12. Industrial tools covered with different hard coatings

In parallel with activities for adapting the deposition technology, a work for adaptation of the electro-discharge polishing process for industrial applications was performed as well. The success in polishing had attracted the attention of many customers and that was the reason to start building such equipment for industrial application of high volume tools. During the project three equipments for electro-discharge polishing were produced. The first one was a prototype with capacity of 7 kW and R&D work of the polishing and deposition processes was performed on it. The second one was semi-industrial with capacity of 20 kW. It was used simultaneously for polishing tools intended for CAD technology and for completing customer orders of low volumes. Using the experience acquired by building the previous equipments and response the needs of clients, third equipment for industrial application with capacity of 30 kW was deigned and produced in the end of the project. The created equipment is used not only for preliminary preparing the tools before coating deposition by CAD technology, but also for execution of orders received from different companies (Remi Ltd., Laserart Ltd. and Comeco Ltd) for tools polishing only. An order from the company TITANIT Ltd., Turkey, for produce and sale of EDP equipment was also received.

As a result of the project objective fulfilment for education and enhancement the research potential, and reinforce the young research potential, a team of scientists and specialists was established. It includes designers of equipment, technologists and specialists on characterization of nanostructured thin films, hard and superhard coatings. By the end of the project tree yang engineers, 5 researchers, 6 Ph.D. students and 6 Doctors have started a work on nanostructured thin films, hard and superhard coatings. The created team will generate added value in respect to strengthening the research capacity of the Innovation centre to the Institute of Applied Physics in the field of nanostructured thin films, hard and superhard coating.

The creation of team for R&D together with the successful improvement of the technology capability of deposition and characterization of nanostructured thin films, hard and superhard coatings as well as adaptation of the technology for industrial applications allowed the reinforce of the existed at IAP Research Centre and its transformation into an Innovation centre for technology, research, education and industrial application. The team experience collected during the work on the project is a prerequisite for the work, performed at the Innovation centre, at a level high enough to be involved into the European scientific society.

QUALITY ASSURANCE OF THE PROJECT IMPLEMENTATION

Project deliverables

The project has 16 deliverables, whose achievement for the all project duration is summarized in Tabl. 2.

The quality assurance of the project was oriented towards achievement of the planed deliverables and a quality control of their fulfilment. The aim of the quality control was to identify deviations from the initial specifications and to undertake the necessary corrective actions. Three stages of quality assurance were used: description, quality control and revision of the deliverables. Deliverables that have passed the quality control and revision were reported and declared as completed and usable.

The quality control of deliverables was realized by checking each deliverable according to its specification and description. The deliverable fulfilment was verified periodically by the management team until its completion.

The revision of deliverables is a non-scheduled change, which could be imposed by the quality control and takes place only if the deliverable under inspection diverges from the quality standards imposed in the description of the deliverable. By the end of the project implementation all deliverables were completed successfully and no deliverable was rejected. The only change was the extension of the deliverable "CD with the presentations at the Workshop II". According to the planed actions it should be completed by making a CD with the presentations at the Workshop NANOHARD 2007 only. However, the interest in taking part in papers, especially by young scientist and doctorants, rose up because of the invitation of the leading scientists and also the participation of new companies paying attention to nanotechnologies. This made necessary the issuing of Proceedings of NANOHARD 2007 because that the presented papers would be considered official publications.

Workshop NANOHARD 2007 was the third scientific event organized by the project team, which had attracted the increased interest. Therefore it was decided to continue the tradition of the forums NANOHARD. The next NANOHARD conference will be held in May 2009.

Table 2. Deliverables of the project

Del. no.	Deliverable name	Work-package no.	Date due	Actual/Forecast delivery date	Estimated indicative person-months	Used indicative person-months per project periods			Lead contractor
						I	II	III	
D1	Founding management team	1	30.06.2005	30.06.2005	0.25	0.25			IAP
D2	Reports of 6 work-meetings in Plovdiv, Bulgaria	1	30.05.2005 30.08.2005 01.06.2006 30.06.2006 30.03.2007 15.09.2007	18.05.2005 20.10.2005 01.06.2006 13.06.2006 29.03.2007 15.09.2007	1.0	0.18	0.6	0.22	IAP
D3	Preparation, web-site creation and report of the International conference	1,3	30.08.2005 30.07.2006 31.01.2007	01.03.2006 30.07.2006 31.01.2007	3.3	1.22	2.08		IAP
D4	Preparation and reports of the workshops in Plovdiv	1,3	30.10.2005 31.07.2007	30.12.2005 31.07.2007	3.2	1.52	0.82	0.86	IAP
D5	Disseminati-on of the results by scientific publications	1	30.09.2007	30.09.2007	0.35	0.14	0.10	0.11	IAP
D6	Project web-site developed	1	30.03.2006	11.07.2005	0.35	0.09	0.26		IAP
D7	Stage I Annual report	1,2,3,4,5	31.03.2006	05.05.2006	3.0	3.0			IAP
D8	Stage II Annual report	1,2,3,4,5	31.03.2007	05.05.2007	3.0		3.0		IAP
D9	Stage III Final report	1,2,3,4,5	30.09.2007	05.11.2007	6.0			6.0	IAP

D10	Report for IAP researcher visit, report for workmeetin	2	30.04.2007	15.09.2007	4.25	1.4	1.54	1.31	IAP
D11	Abook with abstracts of the presentations at the conference	3	30.04.2006 31.01.2007	30.04.2006 31.01.2007	1.0	0.4	0.6		IAP
D12	CD with the presentations at the workshop I	3	30.08.2005 30.10.2005	30.08.2005 30.12.2005	1.0	1.0			IAP
D13	CD with the presentations at the workshop II	3	30.08.2007	30.08.2007	1.0			1.0	IAP
D14	Renovated S&T equipment	4	30.08.2007	30.08.2007	30	13.4	14	2.6	IAP
D15	Definition and evaluation of indicators	5	30.01.2006 30.08.2007	30.01.2006 30.08.2007	5.0	1.4	1.0	2.6	IAP
D16	Revision of deliverables	5	30.03.2007 30.08.2007	30.03.2007 30.08.2007	3.0		1.0	2.0	IAP
				Total :	**65.7**	**24**	**25**	**16.7**	

Project milestones

The successful implementation of the project was assured by the properly definition of the milestones in accordance to the project objectives and deliverables. The milestones were defined for each workpackage and reporting period. The management team controlled their definition and the activities for attaining. The project had 18 milestones, which were attained completely by the end of the project. The list of the project milestones with their achievement is presented in Tabl. 3.

Table 3. Milestones of the project.

Milestone no.	Milestone name	Workpackage no.	Date due	Actual/Forecast delivery date	Lead contractor)
1	Principes,procedures and rules of work agreed upon by the end of the first quarter of Stage 1	WP1	30.06.2005	30.06.2005	IAP
2	Project web site developed to the end of 12 month and permanently updated	WP1	31.03.2006 30.09.2006 30.04.2007 31.09.2007	11.07.2005 01.03.2006 05.03.2007 31.09.2007	IAP
3	Dissemination of the project results after every Report	WP1	30.06.2006 30.06.2007 31.12.2007	30.06.2006 30.06.2007 31.12.2007	IAP

4	Reports to the EC prepared and submitted on time at the end of all Stages	WP1	31.03.2006 31.03.2007 30.09.2007	05.05.2006 05.05.2007 05.11.2007	IAP
5	Choice of appropriate equipment upgrade components for renovation.	WP2	31.08.2005	30.07.2005	IAP
6	Guidance of Ph.D. students in leading European Research Centers.	WP2	31.12.2006 30.04.2007	31.12.2006 30.04.2007	IAP
7	Joint experiments and joint publications	WP2	30.09.2007	30.09.2007	IAP
8	Organization of a conference with national and international impact for enhancement of the research potential	WP3	30.07.2006	28-31.05.2006	IAP
9	Organization of a workshop I with for enhancement of the research potential	WP3	30.08.2005	19-21.10.2005	IAP
10	Organization of a workshop II with for enhancement of the research potential	WP3	31.05.2007	13-16.05.2007	IAP
11	Dissemination of the knowledge by editing of hard and/or electronic proceedings of: d) workshop I e) conference f) workshop II	WP3	30.10.2005 31.01.2007 30.08.2007	20.12.2005 31.01.2007 30.08.2007	IAP
12	Dissemination of the knowledge by reports about: d) workshop I e) conference f) workshop II	WP3	30.10.2005 31.01.2007 30.07.2007	30.12.2005 31.01.2007 30.07.2007	IAP
13	Building and testing the renovated technological equipment	WP4	31.03.2006 31.03.2007	31.03.2006 31.03.2007	IAP
14	Developing technology for nanostructured thin films with new properties	WP4	31.03.2007	31.03.2007	IAP
15	Characterization of the deposition processes	WP4	30.08.2007	30.08.2007	IAP
16	Monitoring system developed and tested	WP5	31.03.2006	28.02.2006	IAP
17	Finalised and tested methods for monitoring and evaluation	WP5	31.03.2007	31.03.2007	IAP
18	Quality control of Workpackage deliverables	WP5	30.09.2007	30.09.2007	IAP

Project indicators

The project indicators revealed the progress of the project during the elapsed period. The following indicators and methods for their measurement were defined:

- *Physical indicators* to measure hard and super hard coatings: thickness, hardness and adhesion. These indicators show the technological reproducibility and degree of the PVD process control. Their evaluation is a measure of the process degree repeatability. The methods used for their measurements and corresponded equipment are described in section "Project objectives fulfilment". The summarized evaluation of the physical indicators measurement showed:
  - Thickness – reproducible (0.5 ÷ 5.0) µm;
  - Rockwell adhesion scale HF (2 ÷ 3) – pass at HF (1 ÷ 4);
  - Composite Microhardness – very good (20 ÷ 37) GPa.
- *Performance indicators* to measure the results obtained in terms of objectives were determined to be:
  - *Increased wear resistance of cutting tools.* This indicator was chosen because the wear resistance should characterize the coatings with respect to their most important application – the increased lifetime of the tools. Usually it is measured by the change in the coating thickness when the tools are subjected to mechanical action during drilling, cutting or turning. The wear resistance of the machining tools has measured by comparing their performance relative to otherwise equivalent but uncoated tools. Companies such as Remi Ltd. and FESTO Ltd. have helped in this respect. TiN protective coatings with thickness of 3 – 4 µm were deposited on steel tools provided by them. Tests performed on these tools under real operation indicated that their lifetime was increased by 2-3 times as compared to uncoated tools.
  - *Renovated multi-functional PVD system suitable for high quality coatings.* This indicator was measured by the capability to grow binary and ternary nitrides suitable for hard and wear resistant tool coatings. This indicator directly correlated with the third project objective. Its measuring showed that the available in the Institute of Applied Physics equipment was renewed and added to in a suitable way so that it can be used to produce quality hard and superhard coatings on various types of instruments made of steel and other materials.
  - *Adaptability level of the upgraded system to industrial application.* The adaptability was evaluated by the achieved capability to deposit the chemical compounds for hard coatings, the reproducibility of the coating deposited upon parts in a single batch and from batch to batch. The orders for deposition of TiN coatings have already been completed for the companies FESTO Ltd., AREXIM Ltd., AFS Ltd. and Remi Ltd. After the end of the project implementation the renovated multifunctional PVD system will be a base for technological transfer to industrial applications.
  - *Improved scientific and educational potential of IAP.* This indicator presents the project implementation progress regarding the improvement of scientific and educational potential of IAP: specialists having prepared their Masters diploma work - expected at least one; Ph.D. students having successfully taken the Doctors minimum exam - at least two within the duration of the project; specialists trained to operate the renovated PVD machine; IAP specialists having visited leading European laboratories and having practiced measurement techniques and participated in cooperative planned experiments; the number of publications in the area of hard and superhard coatings; invited participations of the IAP researchers at scientific forums organized by other scientific

centres.

- Financial indicators to measure the amount of investments to improve the innovation system were defined:
  - *Fixed cost indicator.* This indicator presents the investment costs for upgrading and automation of the existing equipment to a multi-functional PVD system. It includes all costs for purchase of different parts such as vacuum pumps, arc cathodes, a magnetron cathode, heaters and power supply units. The expenses for the needed hardware and software for implementing the full automation of the technological process are also included here. Totally 69781.25 Euro was invested for upgrading and automation of the PVD system. Including the expenses for renovation of the magnetron sputtering equipment and building the EDP equipment, the total sum contributed by EU that is used for equipment is amounting to 79702.65 Euro.
  - *Variable cost indicator.* This indicator presents the investment costs for consumables such as cathode arc coating materials (Ti, Ti-Al, Cr, Zr, etc.), chemicals, gases, pump oils, electric power and water consumption. The variable cost of 23283.28 Euro was invested for consumables for the project implementation.

PROJECT IMPACT

Project's current relation to the state-of-the art

Hard coatings based on transition metal nitrides and carbides are widely used for material protection against wear, abrasion and corrosion. Because of their remarkable properties such as high microhardness, chemical inertness, high wear and abrasion resistance, these coatings have wide application in industry (cutting tools, dies, drills), medicine (instruments, implants, prosthesis), and as decorative tools.

Today three basic types of hard thin film coatings describe the state-of-the art:

(1) single-layered of hard material composition – either a single binary compound or a single-phased solid solution of two or more such miscible compounds. Hardness enhancement may have its origin in two mechanisms – either the chemical nature of the hard material or radiation-induced structural defects causing compressive stress within the coating-substrate system. The achievable hardness is in the range 20 – 40 GPa.

(2) multi-layered superlattice structures consisting of alternating nanometer-sized individual thickness and composition such as to induce stress due to differing elastic moduli and thermal expansion.

(3) nanocomposite bi-phase system consisting of nanometer-sized crystallites embedded into an amorphous matrix of material immiscible with the crystalline phase.

Coating systems belonging to the first two types lose hardness upon defect annealing occurring during the normal operation of the coated machining tools. Hard coatings of the third type are thermally stable up to temperatures in excess of 900-1100°C permitting cutting tool applications in dry machining. Moreover, the nanocomposite systems exhibit superior (than the former ones) hardness reaching values of 70 GPa effectively entering the ultrahardness range and approaching that of layered and bulk crystalline diamond. Hardness enhancement reaches the theoretical limit set for crack-free materials due to size-effect-based blocking of crack nucleation and propagation in nano-crystalline grains. A substantial part of this front-end research is being carried out in EC Research and Educational Centers.

Thin films of types (1) and (3), such as hard coatings based on transition metal nitrides and/or carbides – M(M=Ti, Al)N(C) and novel coatings with improved thermal stability based on dualphase *nc*-M_nN/*a*-Si_3N_4 (M=Ti, W, V...) nanocomposites are an object of our project.

The hardness of our coatings deposited on stainless steel specimens (bulk substrate hardness H = 4 GPa) is in the range 20 – 37 GPa. Absolute hardness was extracted by extrapolation of the composite hardness experimental data measured with varying load. For practical applications the microhardness on coated parts increases 4 to 7.5 times as a result of the TiN coating.

A variety hard and superhard coatings made of nitrides and carbides are prepared by plasma induces techniques, such as plasma chemical vapour deposition (PCVD), cathodic arc deposition (CAD) and reactive sputtering.

After the project fulfilment two techniques, cathodic arc deposition and reactive sputtering are available at the Institute of Applied Physics.

Main achievements as a result of the project implementation

- Acquired know-how and disseminated knowledge on technology and properties of nanostructured thin films, hard and superhard coatings by means of activities with regional, national and international impact were accumulated at IAP. One International conference and two International workshops were organised and held. Their proceedings were disseminated among the participants and the Bulgarian scientists working in this field. Lectures on equipment, technology and characterization were delivered by leading European scientists as gas-visitors at IAP.
- The scientific potential at IAP was enhanced by participation at conferences, workshops, and meetings, by exchange of research visits and joint experiments. New connections with leading European laboratories have been established and a joint work is already caring out. As a result of the collaborations established during the project RTCNANOHARD, joint projects with the Aristotle University and the Institute of Micro and Nanotechnologies of the Technical University of Ilmenau are currently fulfilled.
- The young research potential was reinforced and specialists suited to applied research and further self-improvement have been created by lectures, master and Ph.D. degrees defence and post-doctoral study. Three young engineers and 6 Ph.D. students participated at the team that was established for a work on the project. They will continue to work at the Innovation centre to the Institute of Applied Physics on the same thematic corresponded to the project that provides a good job for them.
- Renovated multi-functional PVD equipment for cathodic arc deposition of hard and superhard coatings is available at IAP. The equipment is completely upgraded and automated, which allows its use not only for scientific R&D and also for fulfilling the large volume customer orders. On this equipment all technologies for coatings were developed. Orders from the companies, FESTO Ltd., AREXIM Ltd., AFS Ltd. and Remi Ltd. have been executed on this equipment presently.
- A specialised system for magnetron spattering was put in operation. It will be used for obtaining nanostructured thin films for special purposes.
- Reproducible technologies for deposition by CAD technique of variety of nitrides, carbides and carbonitrides coatings such as TiN, TiAlN, TiC, TiNC, CrN, ZrN, and TiZrN were developed. Hardness in the range of 20 ÷ 37 GPa have been obtained depending on the coating composition. The technology capability was improved in order to adapt it to industrial applications. As a result a list of recipes was made which allows facile transfer of different coating technologies to the industry. Customer orders for a TiN coating deposited on matrices, dies and knifes are executing presently. The use of these tools in the practice shows that their lifetime increases 2-3 times in comparison with uncoated ones.
- Methodologies for characterization of coating properties such as thickness, hardness,

adhesion, surface morphology, and composition are taken possession by the IAP researchers. The measurements of a thickness and adhesion are performed completely at IAP. The hardness is measured at the Sofia University as our scientists take sufficient part in mathematical processing of the results and determining the composite hardness of the developed coatings. The morphology and composition are investigated in collaboration with our colleagues from the Aristotle University and the Institute of General and Inorganic Chemistry of BAS, respectively.

- Attendant EDP technology and equipment for preliminary preparing the tool surface were developed and applied. They are unique for Bulgaria. The success in polishing has attracted the attention of many customers and that was the reason to start building such equipment for industrial application of high volume tools. Three EDP equipments having capacity of 7 kW, 20 kW and 30 kW were produced during the project.
- As a result of the project implementation the existed Research centre at IAP was reinforced and transformed into an Innovation centre for equipment, technology and characterization of nanostructured thin films, hard and superhard coatings that could provide high level of research, development, education and industrial application in this area of the science and technology.

Criteria for success were used as a measure for the evaluation of the project implementation. They were defined in the beginning of the project. The fulfilment of the project was evaluated by them in the end of each reporting period. Tabl. 4 presents the criteria used for the project fulfilment during the whole project period.

Table 4. Criteria for success during the whole project period.

CRITERION FOR SUCCESS	RELATIVE WEIGHT FOR THE WHOLE PROJECT PERIOD (%)	RELATIVE WEIGHT FOR THE I REPORTING PERIOD (%)	RELATIVE WEIGHT FOR THE II REPORTING PERIOD (%)	RELATIVE WEIGHT FOR THE III REPORTING PERIOD (%)
Strengthening of the research potential as a result of research visits and expressed by investigation experiments, new scientific results and publications.	25	8	14	3
Perform an international conference and workshops.	20	8	9	3
Demonstrate working renovated S&T equipment.	25	15	8	2
Develop and adapt for industrial application of technology for hard and superhard coatings.	10	4	4	2
Working centre for research, development and industrial applications, and education and knowledge dissemination.	20	8	8	4
Total:	**100**	**43**	**43**	**14**

1.2. Dissemination and use

EXPLOITABLE KNOWLEDGE AND ITS USE

The fulfilment of the project provided knowledge in the field of nanostructured thin films, hard and superhard coatings that related to the equipment, deposition technology, film characterization and methodologies used for measurements. The summarized exploitable knowledge concerns the following subjects:

- *Upgrading the basic vacuum system to a PVD system.* The knowledge obtained during the upgrading the available vacuum system into PVD system cover different areas such as: design of new cathodes, skills for cathode and magnetron mounting and mechanical maintenance of whole equipment; design and performance of electrical schemes corresponded to the new cathodes and magnetron; software and automation know-how. As a result specialists in these fields have been created. This knowledge can be applied for R&D work as well as in the industry for technology adapting and production. Documentation for a patent proposal has been prepared and it is in the process of debating.
- *Electro-discharge polishing.* This knowledge relates to both, equipment and technology. It includes all skills for EDP equipment building: design, mechanical and electrical performance. Very important part is the possession of the technology for EDP of different kind of tools. This knowledge has R&D and industrial impact as it is applied for preliminary surface preparation of the tools intended for PVD coatings and also for execution of external orders. The exploitation of the results from electro discharge polishing has generated additional income for IAP.
- *Nitride and Carbide hard and superhard coatings and nitride mixture.* This knowledge is very important because it covers all developed technologies for CAD of metallic nitrides (TiN, CrN, ZrN), carbides (TiC, CrC) and carbonitrides (TiC-TiN, ZrN-ZrC, TiC-ZrN). It is important to point out that one and the same coating cannot be used for each application. A number of factors must be considered prior to selecting a coating for use in particular application. Tool material, heat treatment history, tool function, substrate material, oxidation and corrosion requirements etc. are all important factors determining the proper choice. Therefore, the possession of this knowledge is very important for further R&D of new coating materials as well as in technology transfer in industry and its application for production. The exploitation of this knowledge will have important impact on both the financial state of IAP and its staff (additional jobs). A certificate of invention is being prepared and will be filed at the Bulgarian Patent Office.
- *Nanostructured thin films.* Successfully growing nanostructured thin films suited for superhard coatings on machining tools is considered the culmination of our research and process development. Further collaboration in applied research will be needed after the completion of the project for feasible industrial application. This is the reason to foresee further exploitable results as technological innovation and increased characterization capacity only in the R & D sector after the project end. A certificate of invention is possible but at this stage the work done is considered insufficient. The application for such certificate of invention or know-how will be done after the project expiry.

DISSEMINATION OF KNOWLEDGE

For the whole project duration 13 activities related to knowledge dissemination were foreseen. All of these have been accomplished by the reporting period. Additionally, 7 new activities have been done.

- *National nanotechnology information day.* IAP took part in a national nanotechnology information day named “Micro-and nanotechnology in Bulgaria – development continues”, organized by the Bulgarian Academy of Sciences on 9 June 2005 in Sofia. The project coordinator Dr. Roumen Kakanakov made a presentation of the first results on equipment and technology of hard and superhard coatings.
- *Project web site.* A project web-site www.nanohardbg.com was set up on 11.07.2005 and upgraded periodically up to the end of the project.
- *First International Workshop.* The first International workshop NANOHARD 2005 entitled “Nanostructured Thin Films – Technological Base of a New Generation of Microelectronic Devices and Superhard Coatings” was held in Plovdiv in October 19 to 21, 2005. It was attended by scientists and specialists from 6 countries (Germany, Portugal, Sweden, Greece, Turkey and Bulgaria) and businessmen from Australia and Bulgaria.
- *Book and CD of the first workshop proceeding.* Fifty copies of a book of the International workshop NANOHARD 2005 proceedings were published by December 2005. The ISBN code of the proceedings is 954-9752-44-5. Four of these were sent to the Bulgarian National Library.
- *Direct e-mailing.* A list of Bulgarian and European scientists who work on nanostructured thin films, hard and superhard coatings has been compiled. It contains more than 160 e-mail addresses, which facilitate personal contacts and provide information about the project activities.
- *National exhibition.* The first achievements resulted from this project were shown at an exhibition named „The Bulgarian Academy of Sciences in the European Research Area”. It is worth noting that only institutes having a successful EU project underway were presented there. The exhibition was organized on the occasion of the EU Scientific Research Commissioner Prof. Dr. Janes Potochnik’s inspection of spring 2006 and attended by the Vice-premier and science and education minister D.Vultchev.
- *Advertisement in a magazine.* The Bulgarian Finance magazine published an advertisement of a new hard and superhard coating technology being developed at IAP-BAS Plovdiv in its January-March (No 1, v. III) 2006 issue. An Internet version can be found at www.financebg.com.
- *International conference web site.* A web site about the International conference to be held in Sozopol on May 28 to 31, 2006 was launched. The conference was announced at the web-site address www.nanohardbg.com. After the conference closure this web site was used to disseminate the project achievements after each reporting period.
- *Posters.* In April 2006 six posters in Bulgarian and English languages were designed and exhibited at IAP, Plovdiv and the Bulgarian Academy of Sciences, Sofia for the purpose of advertising the project results.
- *International Conference.* The International Conference NANOHARD 2006 “New Trends in Development of Nanostructured Thin Films, Hard and Superhard Coatings” was held in Sozopol, Bulgaria by May 28-31, NANOHARD 2006 was the second event

organized for dissemination of knowledge and experience in the field of nanostructured thin films, hard and superhard coatings. It was attended by 37 scientists, engineers and specialists from 6 countries: Germany, Portugal, Greece, Turkey, Russia and Bulgaria.

- *Book of International conference proceedings.* The conference presentations were edited and published in Proceedings of the conference and on a CD by January 2007. Their ISBN code is 954-9752-44-5. Four of these were sent to the Bulgarian National Library.
- *Advertisement in a magazine.* The publicity of the project takes the form of on-line advertisement and entry into a business catalogue. The PVD equipment and technology have been advertised in 2006 in an Internet catalogue at a web page www.catalog.bg. For the last six months of 2006 our page impression by the maintainers indicates 1466 visits from 21 countries. An advertisement in a paper edition of the Business Catalogue of the Bulgarian Companies, section Science and Education, p. 285, 2007-2008 was published.
- *International exhibition.* The project results were shown at an International exhibition named „Machines, Technologies, Materials”. The exhibition was organized in the International EXPO Centre, Sofia by the Ministry of Economy by March 28-31 2007. Both Bulgarian and foreign visitors showed their interest toward our hard coating and polishing technologies, among them the manager Yachek Lozinski of "FREUD", Parnow, Poland.
- *Second International Workshop.* The International Workshop NANOHARD 2007 "Development, characterization and industrial application of nanostructured thin films, hard and superhard coatings"was held from 13th to 16th of May 2007 in Velingrad, Bulgaria. The workshop was attended by 33 scientists, engineers and specialists from 8 countries – United Kingdom, Germany, Greece, Switzerland, Belgium, Belarus, Republic of Macedonia and Bulgaria. The workshop was also attended by specialists from 5 industrial companies working in this field: CSM Instruments SA (Switzerland), Plasma Ltd. (Republic of Macedonia), FESTO (Bulgaria), AREXIM (Bulgaria) and Milko Angelov Consult (Bulgaria).
- *Information days.* Informational days were held on May 21-22 2007 at CLAP aimed at popularising the project activities. They were attended by high school and university students, specialists with university degree and representatives of interested firms.
- *Informative Bulletin of BAS.* Information about the NANOHARD 2007 workshop was published in the Informational Bulletin of the Bulgarian Academy of Sciences XII, No 7(113), in its section "News about BAS Units". This bulletin was published in circulation of 500 and sent to all BAS units in Bulgaria.
- *Creating the new IAP web-site.* A new web-site www.clap-bas.com of IAP was created using its own funds in September 2007. It presents the project results up to present days. Information on holding NANOHARD 2007 workshop was published in its special news section. Similarly, the web site will be used to popularise the project activities and the role of EC after the project expiry.
- *International Technical Fair –Plovdiv.* The project team presented its achievements in an exhibition at the International Plovdiv Fair in September 24-30, 2007. Besides the posters, polished stainless steel samples by EDP technology and hard and superhard-coated steel samples were shown at it.
- *CD and Book of the second international workshop proceedings.* The workshop NANOHARD 2007 presentations were edited and published in Proceedings of the workshop in October 2007. A CD edition was prepared and distributed in August 2007.

Fifty copies of the book of the International workshop proceedings under the heading "Development, characterization and industrial application of nanostructured thin films, hard and superhard coatings" were published and four of these were sent to the Bulgarian National Library.

PUBLISHABLE RESULTS

The most important results, obtained from the investigations on nanostructured thin films, hard and superhard coatings developed during the whole project reporting period are presented in 17 papers.

The project team held three events dedicated to education and the dissemination of knowledge where leading European and Bulgarian scientists presented reports:

- 12 papers were reported at the International Workshop NANOHARD 2005 held in Plovdiv, Bulgaria, of which three belong to our project team.
- 20 papers were reported at the International Conference NANOHARD 2006 held in Sozopol, Bulgaria, of which 5 were authored by our project team.
- 17 papers were reported at the International Workshop NANOHARD 2007 held in Velingrad, Bulgaria, of which 7 were authored by IAP staff members.

Some of our results were included in two additional papers at two international forums: one at the International Microscope Congress 2006, Sapporo, Japan and another at the International Conference ECSCRM 2006, Newcastle, UK, the latter published in "Materials Science Forum", 2007 Trans Tech Publications, Switzerland.

Below publications prepared during the whole project period are listed.

1. R.Kakanakov, L.Kolaklieva, *New Cathodic Arc Deposition Equipment and Technology*, Proceedings of International Workshop NANOHARD 2005, Plovdiv, Bulgaria, 19-21 October 2005, ISBN 954-9752-44-5, pp 63-68.

2. Ts.Marinova, R.Kakanakov, L. Kolaklieva, *Formation and Characterization of Metal/SiC Interfaces and Nanostructured Thin Oxide Films*, Proceedings of International Workshop NANOHARD 2005, Plovdiv, Bulgaria, 19-21 October 2005, ISBN 954-9752-44-5, pp 69-77.

3. B.Panayotov, E.Dinkov, *Comparative Overview of Power Supply Units Used as Bias Source for PVD Coating Application,* Proceedings of International Workshop NANOHARD 2005, ISBN 954-9752-44-5, Plovdiv, Bulgaria, 19-21 October 2005, pp 117-120.

4. D. Chaliampalias, G. Vourlias, N. Pistofidis, E.Pavlidou, L. Kolaklieva, R. Kakanakov, I. Tsiaoussis, N.Vouroutzis, E.K. Polychroniadis**,** *Microstructural Study of TiN Coatings with Transmission and and Scanning Electron Microscopy*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, ISBN 954-9752-44-5, pp 11-20.

5. R. Kakanakov, L. Kolaklieva, Chr. Bahchedjiev, T. Cholakova, P. Stefanov, G. Atanasova, *Investigation of the TiN/stainless steel interface obtained by Cathodic Arc Deposition*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, ISBN 954-9752-44-5, pp 27-32.

6. Y.G.Alexiev, Y.V.Baranov, V.A.Burskij, D.S.Domanevskij, S.A.Ivashchenko, V.P.Kazachenko, R.D. Kakanakov, L.P. Kolaklieva, A.A. Kosobutskij, S.I. Moiseenko, A.E. Parshuto, A.V. Stepanenko, *Stainless Steel Surface Modification in Electro-discharge Polishing*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, ISBN 954-9752-44-5, pp 33-36.

7. E.Vlakhov, R.Kakanakov, L.Kolaklieva, Y.Marinov, N.Tonchev, *Ni/NiO Nanodispersed Thin Films : Development and Application*, Proceedings of International Conference NANOHARD 2006, Sozopol, Bulgaria, ISBN 954-9752-44-5, pp 59-62.

8. R. Kakanakov, L. Kolaklieva, E. Dinkov, M. Enevska, *New Electro-Discharge Polishing Equipment***,** Proceedings of International Conference NANOHARD 2006, Sozopol, Bulgaria, ISBN 954-9752-44-5, pp 91-94.

9. D. Chaliampalias, G. Vourlias, N. Pistofidis, L. Kolaklieva, R. Kakanakov, I. Tsiaoussis, V. Kalaitzidis, E.K. Polychroniadis, *Microstructural Study of superhard TiN Coatings with TEM and AFM. An explanation of possible failure***,** Proceedings of the International Microscope Congress 2006, Japan.

10. P.Sveshtarov, R.Kakanakov, L.Kolaklieva, Ch.Bahchedjiev, T.Cholakova, E.Trifonova, Sv.Evtimova, *Microhardness measurement by indentation of TiN, Ti(CN), ZrN, (ZrTi)N hard coatings*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 954-9752-44-5, ISBN 978-954-322-238-4, pp 49-54.

11. D.S.Bobuchenko, Y.A.Bumay, D.S.Domanevskii, R.D.Kakanakov, Y.V.Trofimov, I.A. Horunjii, *Characterization of semiconductor nanosized structures using analysis of electroluminescent spectra, electrical and thermal parameters*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, pp 59-62.

12. M.Milanova, P.Sveshtarov, R.Kakanakov, G.Koleva, B.Arnaudov, S.Evtimova, P.Vitanov, Z.Alexieva, V.Bakardjieva, Ch.Dikov, E.Goranova, *AlGaN/GaAs heterostructures with thin window layer for photovoltaic application*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, pp 75-78.

13. E.Vlakhov, R.Kakanakov, L.Kolaklieva, N.Tonchev, *ALD approach for enhancing sensitivity of porous silicon gas sensors*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, pp 79-82.

14. P. Shindov, R. Kkanakov, Sv. Kaneva, *CdS thin layers deposition by spray pyrolysis,* Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, pp 87-90.

15. R.Kakanakov, Ch.Bahchedjiev, L.Kolaklieva, I.Gradinarski, E.Pashkulov, *Improved Cathodic Arc Deposition System and Technology by Magnetic Controlled Arc Source***,** Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, pp 97-100.

16. B.Panayotov, E.Dinkov, *Comparative overview of gas mixing technology used for PVD coating application***,** Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, ISBN 978-954-322-238-4, p.105-108.

17. L. Kolaklieva, R. Kakanakov, I. Avramova, Ts. Marinova, *Nanolayered Au/Ti/Al Ohmic Contacts to p-Type SiC: Electrical, Morphological and Chemical Properties Depending on the Contact Composition*, Materials Science Forum Vols. 556-557, 2007, pp 725-728.

2. Final plan for using and disseminating the knowledge

Section 1 - Exploitable knowledge and its use

A cumulative overview of the project's undertaken and planned activities is regularly updated at the end of each reporting period. The overview, per exploitable result, how the knowledge could be exploited or used in further research is systemized in Table 1.

Overview Table 1.

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s) of application**	**Timetable for commer-cial use**	**Patents or other IPR pro-tection**	**Owner & Other Partner(s) involved**
1.Upgrading the basic vacuum system to a PVD system	*PVD equipment*	*1. R & D* *2. Industrial application*	*2006* *2007*	*Patent on certain parts of the PVD system is possible*	*IAP Team*
2.Electro - discharge polishing	*Substrate surface polishing*	*1. R & D* *2. Industrial application*	*2006* *2007*		*IAP Team*
3. Nitride hard coatings: TiN, CrN, ZrN, TiAlN	*Cutting instruments, machining tools, ceramics*	*1. Industrial application* *2. Medical Products* *3.Decorati-ve coatings*	*2007*	*Patent application forthcoming*	*IAP Team*
4. Carbide hard and super hard coatings and nitride mixture : TiC, CrC, Ti(N,C)	*Machining tools, cutting instruments, spiral cutting tools*	*1. Industrial application* *2. Medical Products* *3.Decorati-ve coatings*	*2007*	*Patent application forthcoming*	*IAP Team*
5. Nanostructu-red thin films	*Super hard coatings*	*R & D*	*2007 and beyond*	*Know-how and patent*	*IAP Team*

1. Upgrading the basic vacuum system to a PVD system.

The upgrading extends the functionality and capacity of the existing vacuum system converting it into a Physical Vapour Deposition System (PVD). During the first year of the project the basic vacuum system was equipped with two arc cathodes, high capacity substrate planetary holder, two resistant heaters and all necessary power supplies. By the end of the second stage two magnetically controlled cathode arc assemblIes of a new generation were mounted in the PVD machine chamber as planned under item1 and run. These have their complete power supply units with electronic control and accommodate various arc source materials inside. Thus the PVD

equipment has added versatility and functionality that achieves film deposition of better surface smoothness, uniformity, quality and higher growth rate. During the last six months a new process controller was substituted for the existing one. The arc and high voltage power supplies were upgraded and the internal chamber heater received temperature control with feedback replacing the voltage stabilized power supply. The most important step was the purchase of the needed hardware and software for implementing the full automation of the technological process.
A magnetron deposition system to deposit nanostructured superhard coatings was constructed and mounted into a separate vacuum chamber due to difficulties arising from the nature of the two processes, namely the cathodic arc deposition and magnetron sputtering. A specialized input flow automatic valve was purchased to be embedded into a vacuum chamber for layer deposition by magnetron sputtering. This will control and maintain constant reactive gas pressure. Mounting a pulsed magnetron power supply has been foreseen.
The multifunctional PVD system was renovated and used for the production of nanostructured hard and superhard coatings.

The adaptability of the upgraded PVD system to industrial application was evaluated by (1) the achieved capability to deposit the chemical compounds for hard coatings, (2) the reproducibility of the coating deposited upon parts in a single batch and from batch to batch and (3) the ability to run coating services according to a customer's specification. At the end of the project our renovated multifunctional PVD system provides the base for technological transfer to industry.
Documentation for a patent proposal has been prepared and it is in the process of debating.

2. Electrodischarge polishing.
This is an ecological process for polishing substrate surface having many advantages over standard chemical polishing. Its application before the CAD process allows combining all substrate preparations into a single process that makes the method irreplaceable. The result in Stage 1 was used directly by IAP for polishing low volume of substrates needed for R & D work on the arc deposition process. For this purpose prototype equipment was designed and produced from our own resources. This equipment is unique for Bulgaria. A number of commercial contacts have already been made with Remi Ltd., Laser Art Ltd., Comeco and Enginex Ltd., all from Plovdiv, Bulgaria. Presently we are performing polishing for low-volume orders for these.
Our success in electro-discharge polishing during the first stage had attracted the attention of many external customers and was the incentive to start building a second high-volume unit designed for industrial application. During the second stage that unit was constructed and used for high volume coating orders placed by industrial customers.
The exploitation of the results from electrodischarge polishing has generated additional income for IAP and four jobs by the end of the second reporting period.
In response to the increased requirements of our clients, new modernised 30 kW EDP equipment was developed and built. It enables the pre-PVD plasma polishing of larger parts (sized about 600 cm2).
During the whole reporting period IAP has regularly received orders from the companies Laser Art and COMECO, which it has fulfilled. Besides these companies, IAP has received an order from a new client – FESTO, Branch Bulgaria. The exploitation of the results from electro discharge polishing has generated additional income for IAP.

3-4. Nitride and Carbide hard and superhard coatings and nitride mixture.
It is important to notice that one and the same coating cannot be used for each application. A number of factors must be considered prior to selecting a coating for use in particular application. Tool material, heat treatment history, tool function, substrate material, oxidation and corrosion requirements etc. are all important factors determining the proper choice. All considerations already described for nitride coatings are applicable directly to carbides and their

nitride mixtures. Hard coatings of these compositions extend the range of substrate materials and coating specifications.
Various binary and ternary materials obtained by Cathodic Arc Deposition: metallic nitrides (TiN, CrN, ZrN), carbides (TiC, CrC) and carbonitrides (TiC-TiN, ZrN-ZrC, TiC-ZrN) in the thickness range 0,5-5 micron were investigated and evaluated. They were deposited on different types of substrates-stainless steel, high-speed steel, instrumental steel and silicon. The study of the influence of the main deposition parameters (reactive gas pressure, substrate bias, arc current) on the film properties was carried out in order to optimize the cathodic arc deposition process. The hardness of the our coatings deposited on stainless steel specimens (bulk substrate hardness H = 4 GPa) lies in the range 18–37 GPa.
TiN, CrN and ZrN single-layered coatings have passed the research and development stage during the first and second reporting periods and characterization of these has indicated they are ready for industrial application. Ti(NC) and (TiAl)N coatings are under research and development and expected to reach mature state by the end of the project. Many of the technical problems were overcomed in the next project stages. The technology conditions as vacuum pressure, gas ratio, deposition temperature, deposition time, cathode current, affect the coating properties as well. The carbide coatings produced in the second year are still in a stage of research and development.
Different coatings such as TiN, TiCN, AlTiN, ZrN, ZrCN, deposited by Permanent Magnetic Field (PMF) and Controlled magnetic Field (CMF) evaporators have been characterized and compared. Controlled magnetic arc sources produced better coating surfaces with lower concentration of macroparticle inclusions, smoother surface and smaller size of inclusion droplets, twice as small on average as compared to arc sources of permanent magnetic field.
Operating modes to grow optimal coatings are under test and specifying. The Ti(NC) coatings produced by the cathodic arc PVD process have attained hardness and adhesion higher than TiN coatings.
A couple of times Festo's and Remi's orders to deposit a TiN and a wear-resistant Ti (NC) coating on their specimen substrates have been completed. Testing performed at the company's laboratory indicates these coatings' fitness for industrial application.
The need of the Bulgarian market for such coatings now is about 300 000 tools and according to our forecast will grow. As for electro discharge polishing the exploitation of this result will have important impact on both the financial state of IAP and its staff (additional jobs).
A certificate of invention is being prepared and will be filed at the Bulgarian Patent Office.

5. Nanostructured thin films.

Successfully growing nanostructured thin films suited for superhard coatings on machining tools is considered the culmination of our research and process development. As preliminary research in this project has indicated, nanostructured superhard coatings can be deposited by means of either reactive plasma magnetron sputtering or plasma enhanced CVD. The advantages of the first deposition technique over cathodic arc deposition can be summarized as follows: lower chemical contamination, better stoichiometry control, considerably better compositional and thickness uniformity over the whole substrate area.
By the end of the project we have a complete functioning magnetron system mounted in a separate vacuum chamber, with DC power supply, front panel controls, cooling system and gauges. Additionally a second magnetron with AC power supply was incorporated. Thus this system is relatively well outfitted for binary and mixed-binary compound thin film deposition.
After the mounting of the magnetron sputtering system experiments on deposition of nanostructured thin films were performed. The results from microhardness study showed that the process should be optimized. After detailed search it became clear that the magnetron power supply should be replaced by pulsed one to obtain the required coating parameters.
Further collaboration in applied research will be needed after the completion of this project for

feasible industrial application. This is the reason to foresee further exploitable results as technological innovation and increased characterization capacity only in the R & D sector after the project end.
A certificate of invention is possible but at this stage the work done is considered insufficient. The application for such certificate of invention or know-how will be done after the project expiry.

Section 2 – Dissemination of knowledge

For the whole project duration 13 activities related to knowledge dissemination have been foreseen. All of these have been accomplished by the reporting period. Additionally, 7 new activities have been accomplished.
Past activities in dissemination of knowledge generated under the project are summarized in table 2.

Overview Table 2.

Planned/ actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
09.06. 2005	*National nanotechnologys information day*	*Research and higher education*	*Bulgaria*	*120 persons*	*IAP*
11.07. 2005	*Project web-site*	*General public*	*Bulgaria and EC*		*IAP*
19-21 October 2005	*First International Workshop*	*Research, higher education and production business*	*Bulgaria, EC, Turkey and Australia*	*40 persons*	*IAP*
12.2005	*Book and CD of first workshop proceedings*	*Research and higher education*	*Bulgaria, EC, Turkey*	*50 pcs*	*IAP*
April 2006	*Direct e-mailing*	*Research and higher education*	*World wide*	*above 160*	*IAP*
07-14 April 2006	*National exhibition*	*General public*	*Bulgaria and EC*	*300 persons*	*IAP*
March 2006	*Advertisement in a magazine*	*Industrial management and business*	*Bulgaria*	*1000 pcs*	*IAP*
01.03. 2006	*International conference web-site*	*Research and higher education*	*World wide*		*IAP*
April 2006	*Posters*	*General public*	*Bulgaria and EC*	*400 persons*	*IAP*
28-31 May 2006	*International Conference*	*Research and higher education*	*Bulgaria EC, Turkey and Belarus*	*70 persons*	*IAP*
31.01. 2007	*Book of international conference proceedings*	*Research and higher education*	*Bulgaria, EC, Turkey and Belarus*	*70 pcs*	*IAP*

*February 2007 **	*Advertisement in a magazine*	*Science and Education, Production business*	*World wide*	*about 18000 visits*	*IAP*
*28-31 March 2007**	*International exhibition*	*General public*	*Bulgarian and foreign visitors*		*IAP*
May 2007	*Second International Workshop*	*Research, higher education and production business*	*Bulgaria, EC, Turkey*	*30 persons*	*IAP*
*21-22 May 2007 **	*Information days*	*Research and higher education Production business*	*Bulgaria*	*60 persons*	*IAP*
*July 2007**	*Informative Bulletin of BAS*	*Research and higher education*	*Bulgaria*	*500 pcs*	*IAP*
*Septem-ber 2007**	*Creating the new IAP web-site*	*General public*	*World wide*		*IAP*
*24-29 Septem-ber 2007**	*International Technical Fair -Plovdiv*	*General public*	*World wide*		*IAP*
30.08. 2007	*CD of second workshop proceedings*	*Research, higher education and production business*	*Bulgaria, EC, Turkey*	*30 pcs*	*IAP*
*October 2007**	*Book of second international workshop proceedings*	*Research, higher education and production business*	*Bulgaria, EC, Belarus Turkey*	*50 pcs*	*IAP*

**The project knowledge dissemination activities, which have been accomplished additionally.*

National nanotechnology information day

IAP took part in a national nanotechnology information day named "Micro-and nanotechnology in Bulgaria – development continues", organized by the Bulgarian Academy of Sciences on 9 June 2005 in Sofia. The project coordinator Dr. Roumen Kakanakov made a presentation of the first results on equipment and technology of hard and superhard coatings.

Project web-site

A project web-site www.nanohardbg.com was set up on 11.07.2005 and upgraded periodically up to the end of the project.

First International Workshop

The first International workshop entitled "Nanostructured Thin Films – Technological Base of a New Generation of Microelectronic Devices and Superhard Coatings" was held in Plovdiv in October 19 to 21.2005. Leading specialists in the field of hard and superhard coatings from the European Union, Turkey and Bulgaria took part in the workshop, as well as young scientists from IAP and the Technical University of Plovdiv. A doctorant from the Technical University made an oral presentation. The workshop was attended by production businessmen from Australia and Bulgaria. The size of audience was 40 persons.

Book and CD of first workshop proceedings
Fifty copies of a book of the International workshop proceedings under the heading “Nanostructured thin film – technological base of a new generation of microelectronics devices and superhard coatings” were published by December 2005. Their ISBN code is 954-9752-44-5. Four of these were sent to the Bulgarian National Library. CDs with proceedings of the First workshop were sent to interested researchers and industrial business managers.

Direct e-mailing
A list of Bulgarian and European scientists who work on nanostructured thin films, hard and superhard coatings has been compiled. It contains more than 160 e-mail addresses, which facilitate personal contacts and provide information about the project activities.

National exhibition
The first achievements resulted from this project were shown at an exhibition named „The Bulgarian Academy of Sciences in the European Research Area”. It is worth noting that only institutes having a successful EU project underway were presented there. The exhibition was organized on the occasion of the EU Scientific Research Commissioner Prof. Dr. Janes Potochnik’s inspection of spring 2006 and attended by Vice-premier and science and education minister D.Vultchev.

Advertisement in a magazine
The Bulgarian Finance magazine published an advertisement of a new hard and superhard coating technology being developed at IAP-BAS Plovdiv in its January-March (No 1, v. III) 2006 issue. An Internet version can be found at www.financebg.com.

International conference web-site
A web-site about the International conference to be held in Sozopol on May 28 to 31. 2006 has already been launched. The conference has been announced at the web-site address www.nanohardbg.com. After the conference closure this web-site will be used to disseminate the project achievements after each reporting period.

Posters
In April 2006 six posters in Bulgarian and English were designed and exhibited at IAP, Plovdiv and
the Bulgarian Academy of Sciences, Sofia for the purpose of advertising the project results.

International Conference
The International Conference NANOHARD 2006 “New Trends in Development of Nanostructured Thin Films, Hard and Superhard Coatings” was held in Sozopol, Bulgaria by May 28-31. NANOHARD 2006 was the second event organized for dissemination of knowledge and experience in the field of nanostructured thin films, hard and superhard coatings. The Conference was carried out in the frames of the project in response to the needs of the regional and national science and industry. It was attended by 37 scientists, engineers and specialists from 6 countries: Germany, Portugal, Greece, Turkey, Russia and Bulgaria. The conference work was organized in two plenary sessions and one poster session. In the plenary sessions 9 presentations were given and 16 posters during the poster session were presented. Thematically the presentations were distributed in 6 topics: hard coatings and superhard nanocomposite coatings; nanostructured thin film on metals, nonmetals and semiconductors; nanostructured thin films for microelectronics; characterization of thin and nanostructured films; equipment and technology for deposition of hard and superhard nanocomposite coatings; ion plasma cleaning and surface control. Invited talks were given by the leading scientists.

As was written in the foreword to the published proceedings, the success of the International Conference NANOHARD 2006 was due to the high scientific level of the presentations and informal atmosphere of the followed discussions ensured by the session chairmen, as well as the work of many organizers, some "behind the scene".

Book of international conference proceedings

The conference presentations were edited by Dr. Roumen Kakanakov and Dr. Lilyana Kolaklieva and published in Proceedings of the conference and on a CD by January 2007. Four of these were sent to the Bulgarian National Library. Their ISBN code is 954-9752-44-5.
The books of the International conference proceedings were already sent to all participants.

Advertisement in a magazine

Publicity of the project: This takes the form of on-line advertisement and entry into a business catalog. We undertook to advertise equipment and technology in 2006 in an Internet catalog at a web page www.catalog.bg. For the last six months of 2006 our page impression by the maintainers indicates 1466 visits from 21 countries. An advertisement in a paper edition of the Business Catalogue of the Bulgarian Companies, section Science and Education, p. 285, 2007-2008 was published.

International exhibition

The project results obtained during the second reporting period were shown at an International exhibition named „Machines, Technologies, Materials". The exhibition was organized in the International EXPO Center, Sofia by the Ministry of Economy by March 28-31 2007. Both Bulgarian and foreign visitors showed their interest toward our hard coating and polishing technologies, among them the manager Yachek Lozinski of "FREUD", Parnow, Poland.

Second International Workshop

The International Workshop NANOHARD 2007 was the third forum for knowledge dissemination and enhancement of the research potential in the field of nanostructured thin films, hard and superhard coatings, which was organized by the Institute of Applied Physics (IAP) in accordance with the General Workplan of the project RTCNANOHARD. A website of address www.nanohardbg.eu dedicated to this event was created by the 23-rd project month. The workshop was held from 13th to 16th of May 2007 in Velingrad, Bulgaria. The place of the workshop was the Balneological Centre of the Council of Ministers. The presentations were given in the Conference Hall, which was equipped with all multimedia facilities. The poster session was arranged in the conference hall's lobby. The workshop was attended by 33 scientists, engineers and specialists from 8 countries – United Kingdom, Germany, Greece, Switzerland, Belgium, Belarus, Republic of Macedonia and Bulgaria. Invited talks were given by the leading scientists in the field of nanostructured thin films, hard and superhard coatings: Prof. Dr. Dr.h.c. Stan Veprek (Technical University of Munich, Germany), Prof. Steve Bull (Newcastle University, UK) and Dr. Volker Cimalla (Technical University Ilmenau, Germany). Scientists from 7 Research Institutes and 7 Universities participated at NANOHARD 2007. The second workshop became a forum where not only the results from development and scientific study of nanostructured thin films, hard and superhard coatings were present but also the problems of their industrial application were discussed. The workshop was also attended by specialists from 5 industrial companies working in this field: CSM Instruments SA (Switzerland), Plasma Ltd. (Republic of Macedonia), FESTO (Bulgaria), AREXIM (Bulgaria) and Milko Angelov Consult (Bulgaria).

Information days

Informational days were held on May 21-22 2007 at CLAP aimed at popularizing the project activities. They were attended by high school and university students, specialists with university degree and representatives of interested firms.

Informative Bulletin of BAS

Information about the NANOHARD 2007 workshop was published in the Informational Bulletin of the Bulgarian Academy of Sciences XII, No 7(113), in its section "News about BAS Units". This bulletin was published in circulation of 500 and sent to all BAS units in Bulgaria.

Creating the new IAP web-site

A new web-site www.clap-bas.com of IAP was created using its own funds in September 2007. It presents the project results up to present days. Information on holding NANOHARD 2007 workshop was published in its special news section. Similarly, the web site will be used to popularize the project activities and the role of EC after the project expiry.

International Technical Fair -Plovdiv

The project team presented its achievements in an exhibition at the International Plovdiv Fair in September 24-30. Visitors were shown polished stainless steel samples by EDP technology and hard and superhard coated steel samples.

CD and Book of the second international workshop proceedings

The workshop presentations were edited by Dr. Roumen Kakanakov and Dr. Lilyana Kolaklieva and published in Proceedings of the workshop in October 2007. A CD edition was prepared and distributed in August 2007. Fifty copies of the book of the International workshop proceedings under the heading “Development, characterization and industrial application of nanostructured thin films, hard and superhard coatings” were published and four of these were sent to the Bulgarian National Library.

Publishing the Proceedings of Workshop II is not included in the planned activities. However, we decided to edit and publish the presentations for the safe the high interest in the workshop subjects demonstrated by the scientific community and the companies working in the same field.

Books of the Second International Workshop proceedings were already sent to all participants.

Section 3 - Publishable results

The most important results, obtained from our investigation in the field of nanostructured thin films, hard and superhard coatings developed during the whole project reporting period are presented in 17 papers.

The project team held three events dedicated to education and the dissemination of knowledge where leading European and Bulgarian scientists presented reports:

12 papers were reported at the International Workshop “NANOHARD 2005” held in Plovdiv, Bulgaria, of which three belong to our project team. 20 papers were reported at the International Conference “NANOHARD 2006” held in Sozopol, Bulgaria, of which 5 were authored by our project team. 17 papers were reported at the International Workshop “NANOHARD 2007” held in Velingrad, Bulgaria, of which 7 were authored by Institute of Applied Physics staff members.

Some of our results were included in two additional papers at two international forums: one at the International Microscope Congress 2006, Japan and another at the International Conference “ECSCRM 2006”, Newcastle, UK, the latter published in ”Materials Science Forum”, 2007 Trans Tech Publications, Switzerland.

The list of publications prepared during the whole reporting period is as follows:

1. R.Kakanakov, L.Kolaklieva, *New Cathodic Arc Deposition Equipment and Technology*, Proceedings of International Workshop NANOHARD 2005, Plovdiv, Bulgaria, 19-21 October 2005, pp 63-68.
2. Ts.Marinova, R.Kakanakov, L. Kolaklieva, *Formation and Characterization of Metal/SiC Interfaces and Nanostructured Thin Oxide Films*, Proceedings of International Workshop NANOHARD 2005, Plovdiv, Bulgaria, 19-21 October 2005, pp 69-77.
3. B.Panayotov, E.Dinkov, *Comparative Overview of Power Supply Units Used as Bias Source for PVD Coating Application,* Proceedings of International Workshop NANOHARD 2005, Plovdiv, Bulgaria, 19-21 October 2005, pp 117-120.
4. D. Chaliampalias, G. Vourlias, N. Pistofidis, E.Pavlidou, L. Kolaklieva, R. Kakanakov, I. Tsiaoussis, N.Vouroutzis, E.K. Polychroniadis**,** *Microstructural Study of TiN Coatings with Transmission and and Scanning Electron Microscopy*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, pp 11-20.
5. R. Kakanakov, L. Kolaklieva, Chr. Bahchedjiev, T. Cholakova, P. Stefanov, G. Atanasova, *Investigation of the TiN/stainless steel interface obtained by Cathodic Arc Deposition*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, pp 27-32.
6. Y.G.Alexiev, Y.V.Baranov, V.A.Burskij, D.S.Domanevskij, S.A.Ivashchenko, V.P.Kazachenko, R.D. Kakanakov, L.P. Kolaklieva, A.A. Kosobutskij, S.I. Moiseenko, A.E. Parshuto, A.V. Stepanenko, *Stainless Steel Surface Modification in Electro-discharge Polishing*, Proceedings of International Conference NANOHARD 2006, Zosopol, Bulgaria, pp 33-36.
7. E.Vlakhov, R.Kakanakov, L.Kolaklieva, Y.Marinov, N.Tonchev, *Ni/NiO Nanodispersed Thin Films : Development and Application*, Proceedings of International Conference NANOHARD 2006, Sozopol, Bulgaria, pp 59-62.
8. R. Kakanakov, L. Kolaklieva, E. Dinkov, M. Enevska*, New Electro-Discharge Polishing Equipment***,** Proceedings of International Conference NANOHARD 2006, Sozopol, Bulgaria, pp 91-94.
9. D. Chaliampalias, G. Vourlias, N. Pistofidis, L. Kolaklieva, R. Kakanakov, I. Tsiaoussis, V. Kalaitzidis, E.K. Polychroniadis, *Microstructural Study of superhard TiN Coatings with TEM and AFM. An explanation of possible failure***,** Proceedings of the 16th International Microscope Congress 2006, Sapporo, Japan.
10. P.Sveshtarov, R.Kakanakov, L.Kolaklieva, Ch.Bahchedjiev, T.Cholakova, E.Trifonova, Sv.Evtimova, *Microhardness measurement by indentation of TiN, Ti(CN), ZrN, (ZrTi)N hard coatings*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp 49-54.
11. D.S.Bobuchenko, Y.A.Bumay, D.S.Domanevskii, R.D.Kakanakov, Y.V.Trofimov, I.A. Horunjii, *Characterization of semiconductor nanosized structures using analysis of electroluminescent spectra, electrical and thermal parameters*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp 59-62.
12. M.Milanova, P.Sveshtarov, R.Kakanakov, G.Koleva, B.Arnaudov, S.Evtimova, P.Vitanov, Z.Alexieva, V.Bakardjieva, Ch.Dikov, E.Goranova, *AlGaN/GaAs heterostructures with thin window layer for photovoltaic application*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp 75-78.

13. E.Vlakhov, R.Kakanakov, L.Kolaklieva, N.Tonchev, *ALD approach for enhancing sensitivity of porous silicon gas sensors*, Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp 79-82.

14. P. Shindov, R. Kakanakov, Sv. Kaneva, *CdS thin layers deposition by spray pyrolysis,* Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp.87-90.

15. R.Kakanakov, Ch.Bahchedjiev, L.Kolaklieva, I.Gradinarski, E.Pashkulov, *Improved Cathodic Arc Deposition System and Technology by Magnetic Controlled Arc Source***,** Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp.97-100.

16. B.Panayotov, E.Dinkov, *Comparative overview of gas mixing technology used for PVD coating application***,** Proceedings of International Workshop NANOHARD 2007, Velingrad, Bulgaria, 2007, pp 105-108.

17. L. Kolaklieva, R. Kakanakov, I. Avramova, Ts. Marinova, *Nanolayered Au/Ti/Al Ohmic Contacts to p-Type SiC: Electrical, Morphological and Chemical Properties Depending on the Contact Composition*, Materials Science Forum Vols. 556-557, 2007, pp 725-728.

The publications directly related to the project subject and authored by the IAP staff members are presented below:

New Cathodic Arc Deposition Equipment and Technology

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Keywords: nanostructures, cathodic arc deposition, hard coatings, superhard coatings.

Abstract. Nanostructured thin films, hard and superhard coatings based on transition metal nitrides and carbides are widely used today to protect materials against wear, abrasion and corrosion. Due to their remarkable properties such as high microhardness, chemical inertness, high wear and abrasion resistance, these coatings are employed in various machining applications to improve the performance of tools and mechanical components.

These coatings are usually obtained by different PVD techniques: magnetron sputtering, cathodic arc deposition, MBE, laser deposition. To achieve our aims, namely research, development and industrial application of nanostructured thin films, hard and superhard coatings, we chose cathodic arc deposition technique. This technique allows obtaining qualitatively controlled films and has a high output. We started building the cathodic arc deposition equipment together with the Stevac Ltd. company in the framework of a FP6 European project. The first stage of the building is complete. At this workshop we are presenting working equipment consisting of a vacuum chamber with two cathodes and automatic control of the process.

To test the equipment, coatings of TiN, CrN and (TiAl)N with a thickness of 1 μm and a microhardness of the order of 3 GPa were obtained.

The second stage of equipment construction, which is in progress, will expand its resources including two new cathodes and one magnetron.

Introduction

Nanostructured thin films, hard and superhard coatings based on transition metal nitrides and carbides are widely used today to protect materials against wear, abrasion and corrosion. Due to their remarkable properties such as high microhardness, chemical inertness, high wear and abrasion resistance, these coatings are employed in various machining applications to improve the performance of tools and mechanical components.

Films like TiN, TiC, ZrN, Ti(C,N), (Ti,Zr)N and (Ti,Al)N have mostly been used for hard coatings deposited on Si, stainless steel and high-speed steel substrates [1-4]. Alternate TiN/ZrN and other multilayers have also been applied by some authors as hard coatings [5, 6]. Recently, nanostructured coatings have increasing interest because of the possibility of synthesizing materials with unique physical and chemical properties [7-9]. Highly sophisticated surface related properties, (optical, magnetic, electronic, catalytic, mechanical, chemical and tribological) can be obtained by advanced nanostructured coatings, making them attractive for industrial application in high-speed machining [10, 11], tooling [11, 12], optical applications [13, 14], and magnetic storage devices [15-17], because of their special properties due to the size effect.

Until recently, coatings with a hardness of 3 – 4 GPa were considered as hard coatings. Recently, coatings with hardness even of about 20 GPa were also determined as hard. Above 40 GPa the coatings are classified as superhard and those with a hardness above 70 GPa are often called ultra-hard coatings.

To design nanostructured coating, one has to consider many factors, e.g. interface volume, crystallite size, single layer thickness, surface energy, texture and etc., all of which depend significantly on materials selection, deposition methods and process parameters [18, 19]. There are many types of design models for nanostructured coatings such as nanocomposite coatings, nano-scale multilayer coatings, superlattice coatings, nanograded coatings, etc.

Nanocomposite coatings are very promising because they exhibit a hardness significantly exceeding that given by the rule of mixture. A nanocomposite coating comprises at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. Nanocomposite coatings can be hard, superhard or even ultra-hard, depending on coating design and application.

Various deposition techniques have been used to prepare different hard, superhard and ultra-hard coatings. Among them cathodic arc deposition (CAD) and reactive magnetron sputtering are most commonly used.

I. Development and fabrication of Cathodic Arc Deposition equipment

It is known that the ionization efficiency of the metal vapor in arc discharge reaches more than 70% and in some cases it increases to 90%. Taking into consideration this fact, we have chosen to use Cathodic Arc Deposition (CAD) equipment for developing our coatings. The high ionization efficiency of the CAD process exceeding that of other PVD processes enhances the coating adhesion and density. Besides, the CAD process has high productivity.

Since the CAD systems offered on the market are very expensive (between 600 000 and 700 000 EUR) and do not combine the possibilities of manufacture with R&D work, we have chosen to construct such equipment by ourselves. Our work was based on utilization of parts offered on the market and original parts produced by us together with the company STEVAC Ltd., which has experience in this respect.

Thus our activities on the development and fabrication of CAD equipment, were directed towards: 1) marketing and purchasing units, such as mechanical, acceleration and diffusion pumps, traps valves, vacuum meters, mass-flow controllers, pure gases (Ar, N, CH_4), pure metals for cathodes (Ti, Al, Cr, Zr), which could not be made either by our Institute or by STEVAC Ltd., and 2) fabrication by the Institute of Applied Physics and STEVAC Ltd. of units such as vacuum chamber with special cooling, planetary rotation system, arc sources, power supply, process controllers. The principle scheme of the developed Cathodic Arc Deposition equipment is presented in Fig. 1. The vacuum chamber with a planetary rotation system has a capacity of 500 l. It is made of stainless steel with a double wall for water cooling. Two cathodes are mounted on the vacuum chamber wall at present. For obtaining multilayer structures of different metals, two more cathodes with screens will be installed. To improve the equipment possibilities, a magnetron with a RF power supply will also be mounted.

The fixture system, including a planetary rotation system for racks, is mounted inside the chamber. The planetary rotation system supports several fixture posts and is driven by a variable-speed motor. It provides two degrees of motion for each of the fixture posts, self-spinning as well as circling around the chamber. Consequently, an uniform coating is achieved.

A bias power supply with controller provides electrical potential bias between the cathodes and the substrates. As a result, the charged particles emitted from the cathodes will gain acceleration from the electric field and deposit onto the substrate with a high kinetic energy. This kinetic energy turns into bonding power, which ensures good adhesion. Local area arcing due to out-gassing on the substrate surface during deposition may damage the quality of the coating. To minimize local area arcing, the bias power controller must have an arc suppression system. Such a bi-polar arc suppression system with pulse mode is developing. Its main parameters are:

- Output voltage – to ± 1000 V;
- Output current – average 15 A;
- Output current – maximum 150 A;
- Time for suppression within $T_{arc} \leq 2$ μs.

An arc-power-circuit-supply controller has as many sets of controllers as are the cathodes, one for each cathode. Three parameters are displayed and can be adjusted: the current of the cathode, an arc restarted with automatic restart circuit, and water-cooling for cathodes. The voltage between anode and cathode is in the range 20 – 100 V depending on the anode-cathode configuration and the cathode material.

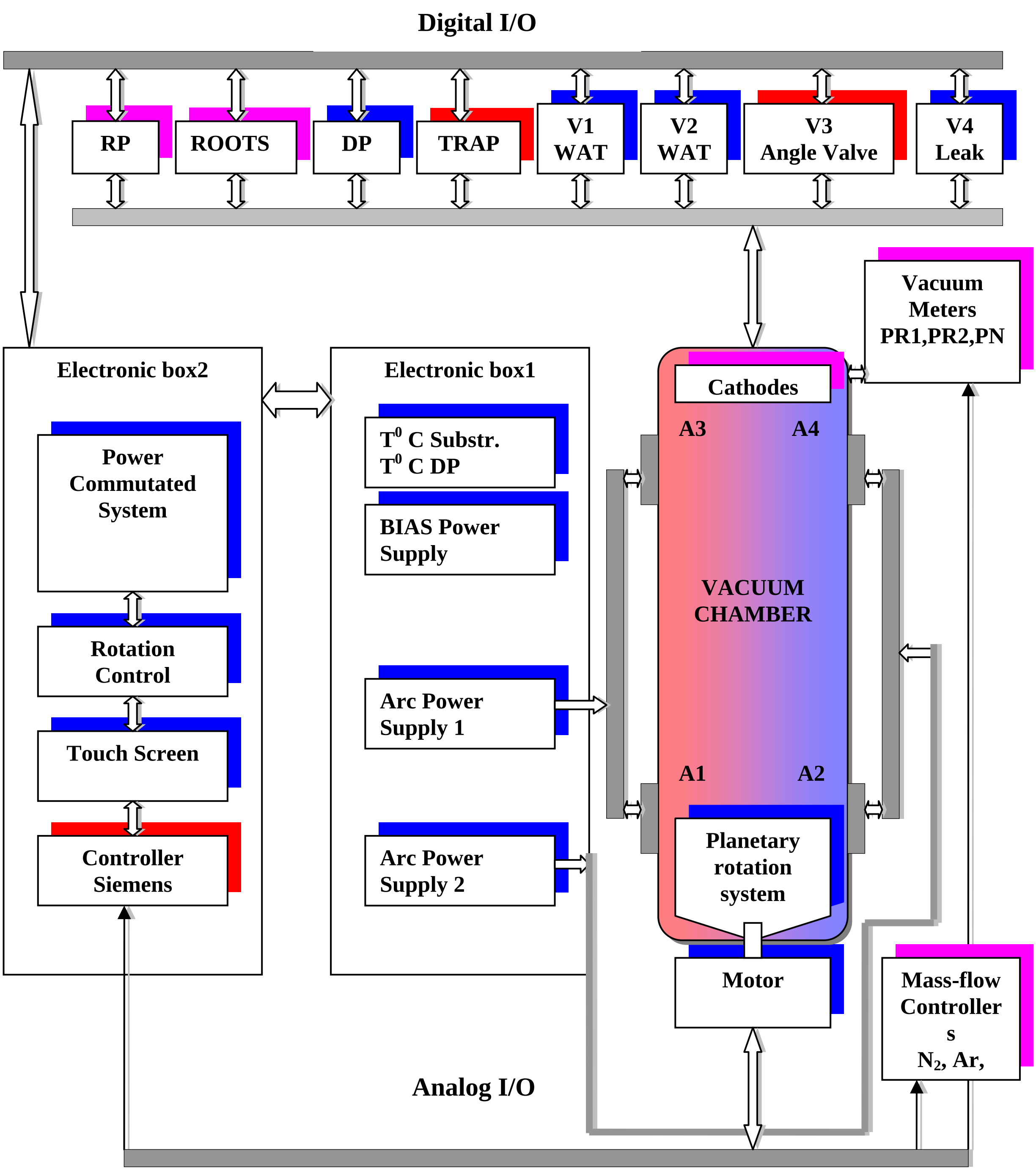

Fig. 1. *Principle scheme of the Cathodic Arc Deposition equipment for hard coatings:* ***RP*** *– rotation pump,* ***ROOTS*** *– acceleration pump,* ***DF*** *– diffusion pump,* ***V1-V4*** *– vacuum valves,* ***A1-A4*** *– vacuum chamber inputs,* ***PR1, PR2, PN*** *– vacuum meters*

A photograph of our CAD equipment is presented in Fig. 2.

Fig. 2. *Photograph of the Cathodic Arc Deposition equipment for hard coatings*

II. Development and application of a technology for Cathodic Arc Deposition of hard coatings

Cathodic Arc Deposition (CAD) is a branch of the physical vapour deposition technology used for obtaining coatings. It is a vacuum plating technique where metal vapour in highly ionised plasma is generated by use of electric arcs. This method offers a wide range of possibilities for the modification of deposition parameters. It permits deposition of high melting metals and compounds onto different materials such as steel, hard metals, plastic, ceramic, glass and etc., as the materials can be deposited with improved properties to the substrate material.

The first results obtained on the developed CAD equipment are presented in Table 1.

Table 1. *Main parameters of the developed coatings.*

COATING	THICKNESS [μm]	HARDNESS [GPa]	ADHESION
TiN	0.5 – 3	15 – 25	excellent
CrN	0.5 – 1	20 – 24	excellent
ZrN	0.5 – 1	18 – 24	excellent

Figure 3 illustrates different industrial applications of a TiN hard coating: for cutting tools, decorative tools, medical instruments and etc.

Fig. 3. *Photograph of different tools with a TiN hard coating*

Summary

- The developed equipment for Cathodic Arc Deposition is a modern equipment, which combines a production process with possibilities for R&D work and allows further upgrade.
- The basis of flexible technology for cathodic arc deposition of hard and superhard coatings is created.
- Methods for evaluation of the coating quality are developed.

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Microstructural Study of TiN Coatings With Transmission and Scanning Electron Microscopy

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Keywords: Cathodic Arc, Hard Coatings, TiN, Electron microscopy

Abstract. Superhard TiN coatings have attracted considerable attention due to their hardness, which is in the range of diamond. The properties of these coatings are highly affected by the deposition method and the growth conditions. In the present work, TiN was deposited on stainless steel (SS420) using cathode-arc deposition method and the effect of the N_2 flow and the deposition temperature on the coating microstructure and thickness was studied. For that purpose Scanning Electron Microscopy (SEM) and Transmission Electron microscopy (TEM) were used. From TEM examination it was deduced that the coating is composed of grains of different sizes, grown by the columnar growth mode. When Ar is inserted in the chamber, the stoichiometry of TiN is not constant but it ranges from $TiN_{0.76}$ to $TiN_{0.98}$. Furthermore in some of the crystals a preferential growth direction [111] is observed. Moreover the grain size depends on the temperature as larger grains were measured at high deposition temperatures. SEM examination showed that the coating surface is not homogeneous because droplets of TiN along with craters are present. As a result thickness variations are expected at larger scale examination of the coating. However the droplets are reduced and the craters size is also reduced as the N_2 flow increases. Also the low vacuum in the coating chamber and rough surface of the substrate can cause the creation of sparks between anode and cathode which results to rough and bad quality coatings.

Introduction

Stainless steels are widely used in industry due to their high mechanical properties and corrosion resistance. Fast pace engineering and manufacturing technology brings the necessity for increasing requirements to the contemporary sintered tool materials focusing on their working properties. Deposition of hard wear resistance coatings based on carbides, nitrides, or transition metals oxides, features one of the fastest developing directions of research today. Influenced by the growing function requirements of machines and equipment, especially in the metal forming, machining and plastic manufacturing industry makes definite improvement on the sintered tool materials (sintered high speed steels, cemented carbides, cermets, ceramics).

Nowadays there are numerous types of coatings available and a variety of technologies for their deposition. Special interest is gathered on coatings which associate multiple properties like wear and corrosion resistant coatings. Steels covered by coatings based on carbides, borides, nitrides, and oxides are generally known to work at higher function parameters (temperature, load, etc.). Between them metal nitrides have many unique properties and are widely used as industrial coatings. The reason is that they combine many properties which can fulfil the demands of contemporary industry, such as low friction, surficial hardness and corrosion resistance instead of one particular quality. Titanium nitride (TiN) films are widely used on multiple industrial accessories in many applications in order to ameliorate their surficial mechanical properties such as high abrasion resistance, low friction coefficient, high temperature stability and high durability of metallic cutting tools [1]. Hardness in particular can be increased in the range of diamond by the application of such coatings [2-4].

Up to now there have been multiple methods of depositing TiN such as reactive unbalanced magnetron (UBM) sputtering [5], chemical vapour deposition methods [6], plasma vapour deposition method [7], plasma-enhanced chemical vapour deposition PECVD [8] ion-beam-enhanced deposition (IBED) technique [9] and several physical vapour deposition (PVD) processes [10]. In the present work TiN films were deposited on stainless steel with the Cathodic Arc deposition technique under various conditions. With this technique coatings with excellent adhesion to the substrate and with all the previous mentioned features [11-13] are formed. The effect of the nitrogen flow rate and the deposition temperature on the structure and the thickness of the as formed coatings is also examined. This investigation deals with the factors that can affect the mechanical properties of the as formed TiN films such as the microstructural characteristics of the coating grains, the presence of different TiN phases and the film thickness [14-20]. The combined study of the structure and the processing parameters is very important in order to configure the optimum conditions for the formation of high quality coatings.

Experimental

In the present work commercial stainless steel AISI 420 was used as substrate. Prior to the coating process, the substrates were ultrasonically cleaned in acetone and ethanol and then dried. During the main coating procedure the surface of the samples was cleaned using stream of Ti^{2+} ions in a vacuum chamber (10^{-5} mbar) at high voltage (~1000 V). This high voltage produces an electrical breakdown in the chamber. During the breakdown electrons are separated from their host N_2 atoms creating plasma. Metal ions are generated by electron impact ionization ($e^- + M \rightarrow M^+ + 2e^-$) and by Penning ionization by collision with a metastable excited Ar atom ($Ar^* + M \rightarrow M^+ + Ar + e^-$) [21]. The vacuum arc is a high current, low voltage discharge between a pair of electrodes located in a vacuum chamber. The electrical current is carried by the plasma produced by ionizing material (Ti^+) which the arc evaporates from the electrodes. Afterwards, a negative voltage of 150 V was applied to the substrates in order to increase the Ti^{2+} energy and orientate their flow. Under these conditions the ionized reactive gas (N_2) reacts with the Ti ions forming TiN, which are deposited onto the surface of the substrate. The average temperature of the substrate is 350^{o}C at the beginning of the process while the deposition temperature varies. The experimental parameters which were followed are listed in table I.

The surface examination of the coating was performed by scanning electron microscopy (SEM) using a 20kVolt JEOL 840A SEM and Atomic Force Microscopy (AFM) using a Topometrix Explorer 200 AFM. The microstructural characterization of the as-formed coatings was performed by Transmission Electron microscopy (TEM) using a 100kV JEOL 100CX TEM.

Table I – List of samples and experimental conditions

Sample	N_2 flow [sccm]	Ar flow [sccm]	Pressure [mbar]	Deposition Temperature (^{o}C)
1	300	77	3x10-3	290
2	300	0	1.3x10-3	290
3	400	0	3.6x10-3	240
4	500	0	6x10-3	305
5	300	169	6x10-3	262

Scanning electron microscopy as well as Atomic Force microscopy gives a direct image of the surface in order to study the surface morphology of the coating. Transmission electron microscopy is the best technique for the study of the microstructure. By combining bright and dark field plain view images and electron diffraction, it is possible to obtain information on the existing phases, the grain size and shape, if there is a preferred orientation and the kind and the density of the structural defects, if any, due to the limited grain size. Additionally by cross-sectional observation it is possible to obtain information on the growth mode, the evolution of the growth, the substrate/coating interface, as well as the exact thickness of the coating. Of course there are always limitations, due to the very limited area of observation. It is also necessary to emphasize here the existing difficulties in TEM specimen preparation, especially for the cross sectional samples. The difficulties arise from the large differences in the ion milling rates, between the coating and the substrate and the highly stressed material as well.

Results – discussion

1. Failure analysis

During the deposition process some of the experimental parameters varied driving to coating failure which was also visually observed as different (more blur) coloration of the final product. A crucial parameter in order to ensure good quality is to keep the vacuum of the chamber at 10^{-5} mbar in order to obtain a smooth substrate with low roughness during the high voltage cleaning. The existence of lower vacuum results to the appearance of sparks which are produced at the anode of the setup (Ti source) and the cathode (the rougher areas of the substrate). These sparks are created during the secondary cleaning, performed in the coating chamber, when the high bias (1000V) is applied in order to bomb the substrate surface with Ti^{2+} ions. The sparks probably cause the local melting of the substrate resulting to the change of its structure. Those areas, as it was proved experimentally, are not favourable for TiN growth.

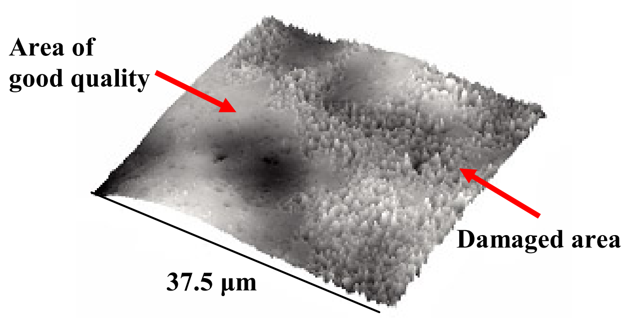


Fig. 1. AFM micrograph showing the different appearance of the good and the damaged areas.

The as referred areas were firstly examined with AFM (Fig.1). From this micrograph areas where TiN growth was accomplished normally seem to be much smoother than those where the substrate was locally melted and the surface is very rough.

In figure 2 a TEM plain view micrograph of a normal grown coated area (fig. 2a) is presented together with the micrograph of a damaged area (fig. 2c). In the normal surface TiN grains are observed on the surface of the coating. In the case where the coating is damaged, because of the bad experimental conditions, we can also observe TiN grains but there is also a thin nanoparticle layer of austenite with Cr. The presence of these phases was detected by the ED patterns taken from the same areas of the coating. In the ED pattern of fig. 2b the rings corresponding only to the polycrystalline TiN phase are clearly visible. The ED pattern

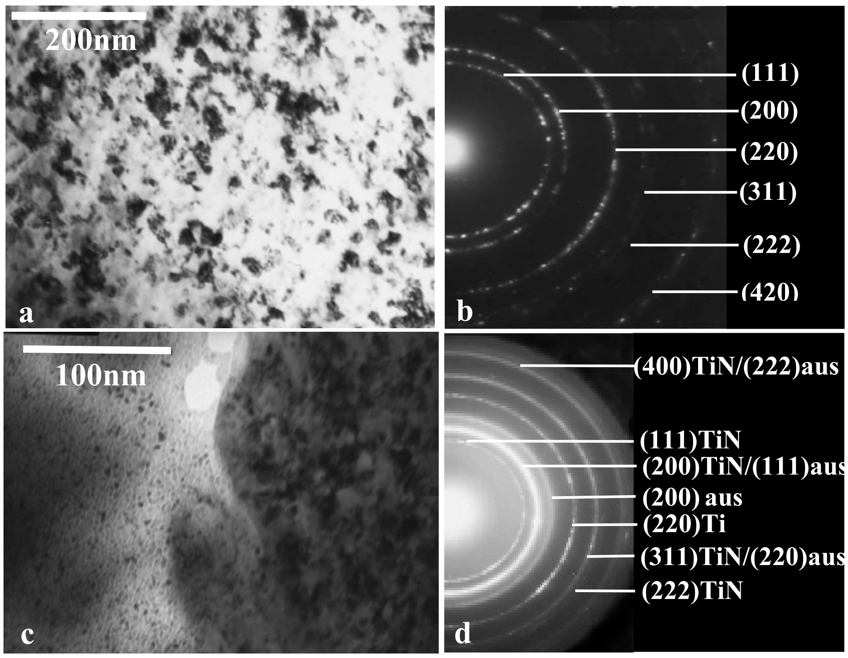


Fig. 2. TEM plain view micrographs and corresponding ED patterns of the normal (a, b) and the damaged area (c, d) of the coating.

of fig. 2d consists of the previously mentioned polycrystalline TiN rings as well as a nanocrystalline set of rings belonging to the austenite phase (fig.2c, 2d).

In order to have a better visualisation of the structure of the damaged area cross sectional samples for TEM observation were prepared and the corresponding bright field TEM micrographs are presented in figure 3. In the micrograph of fig. 3a the columnar growth of the TiN grains is clearly presented in comparison with the TEM micrograph of fig. 3b where the columnar growth of TiN grains is hardly distinguished above the austenite nanoparticle layer, which is in contact with the substrate.

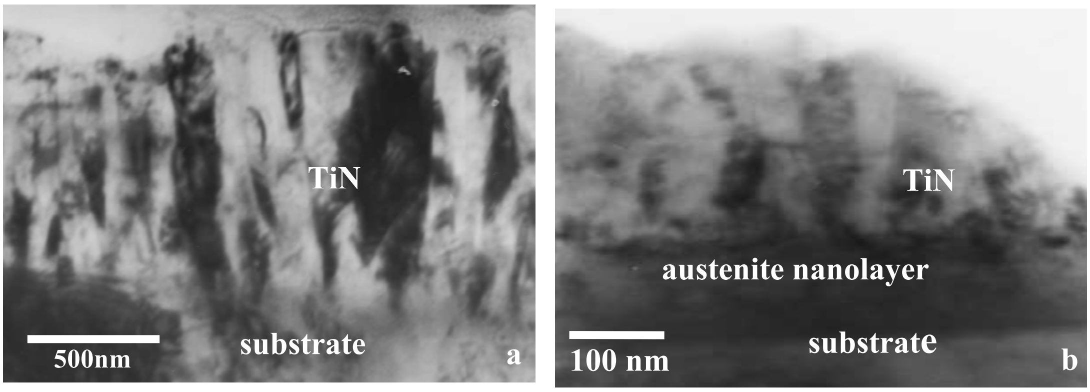


Fig. 3. Cross-sectional bright field TEM micrograph of the normal coating (a) and the damaged area (b).

2. Substrate characterization

In order to verify the results from the failure analysis the substrate was observed and characterized by TEM. The as examined substrate was taken from the coating chamber right after the secondary cleaning and before the main coating procedure. During this secondary cleaning, as it is already mentioned in the experimental part of this work, the substrates are bombarded with Ti^{2+} ions, so the characterization of the substrate is necessary in order to record any structure modification during this process.

Fig. 4 presents an ED pattern taken from a plain view oriented sample. This was prepared after thinning (ion milling) only from the back side of the sample in order to have the surface untouched and this way to get all the available information. bright field plain view of the surface of the substrate. This ED pattern consists of two easily distinguished phases. One consists of large individual spots indicating large grains and the other of complete rings indicating a nanocrystalline material. Accurate measurements revealed that the sots correspond to the substrate phase Fe_xCr_{1-x}, where x ranges from 0 to1 and the rings to iron oxide FeO_y with y ranging from 0.911 to 0.987. The presence of the oxide is not attributed to the inadequate cleaning of the substrate but to its immediate oxidation after its taking out from the vacuum chamber. Also it must be mentioned that there was not any Ti traced on the substrate.

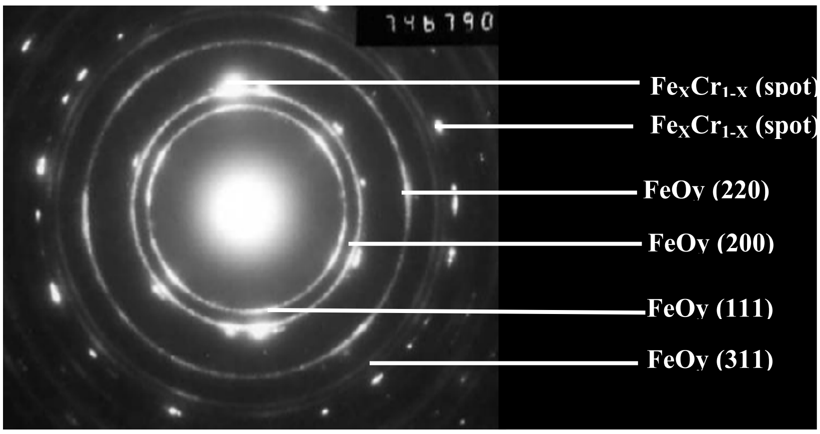


Fig. 4. TEM plain view micrograph and corresponding ED pattern of the cleaned substrate.

3. Surface quality

The examination of the surface of the coatings was performed with SEM. The observations revealed that the surface of TiN coatings is rather smooth although there are numerous droplets and craters spread all over the coating surface. These are easily seen in the SEM micrograph of fig. 5. EDS analysis accomplished on these features showed that the droplets are composed of pure TiN, while in the craters a lack of coating elements is observed. As a result mainly Fe originating from the substrate is detected. These remarks are also proved from chemical mapping of the same areas (fig. 6 and 7).

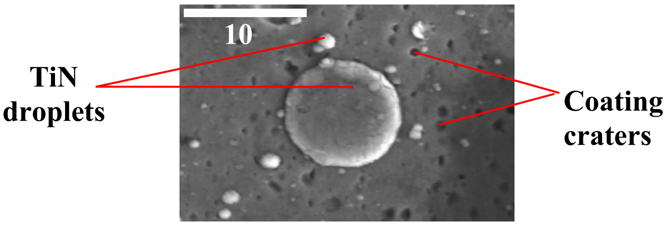


Fig. 5. SEM micrograph of the coating surface with TiN droplets together with craters.

The droplets are formed during the arc discharge as small liquid Ti microparticles are created from the cathode surface which also react with N_2 forming a TiN shell around the Ti core. Once the microparticle collides with the TiN coating and stays on the surface, voids beneath are formed. After a short period the flattened voids are sealed as the deposition continues but voids near the coating surface result in poor adherence of the microparticle to the coating. These microparticles may easily crack leaving craters when used at any mechanical application. Also the electrical charge accumulated on the Ti droplets while passing through the plasma area and the internal stresses, may result in the repulsion of the microparticle by the high biased substrate and its debonding due to the difference in the thermal expansion coefficient between the core Ti and the TiN shell, leaving again pinholes and craters on the coating surface. As a result wear and corrosion resistance of the coating is weakened as small areas of the substrate are exposed to corrosive working environments. To avoid the formation of the as referred droplets particular filters are used which capture the Ti microparticles [22].

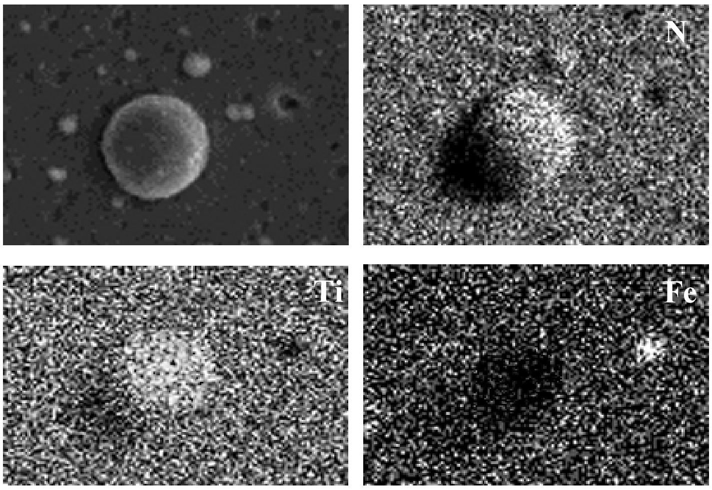


Fig. 6. Chemical mapping of the TiN droplets.

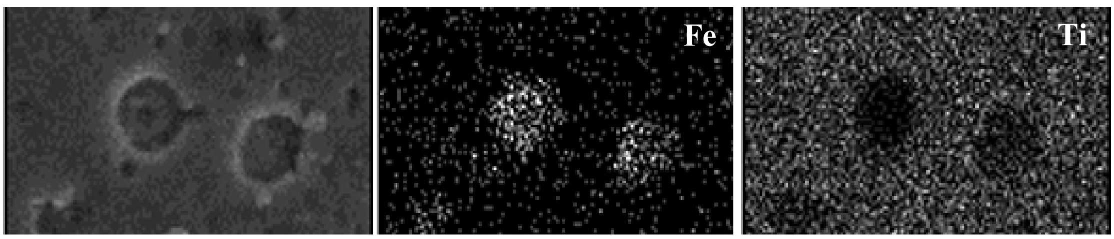


Fig. 7. Chemical mapping of an area with craters.

4. The effect of N_2 flow and deposition temperature on the coating

At the beginning, the samples, coated under the experimental conditions listed in table I, were examined by SEM (fig. 8). All of them have TiN droplets and craters on its surface. But we can safely claim that as the N_2 flow in the deposition chamber increases, the droplets tend to decrease.

Especially in the case of sample 3 and 4 their presence is very rare. Samples 1,2,5 have similar surface morphology as there were equal nitrogen flows during their deposition. Also the areas with craters tend to increase in number and decrease in size with the rise of N_2 flow in the coating chamber. The presence of craters, on the surface, can be explained as the increased N_2 flow in the vacuum chamber induces much more stressed in the as formed films making more droplets to crack and form craters at their place.

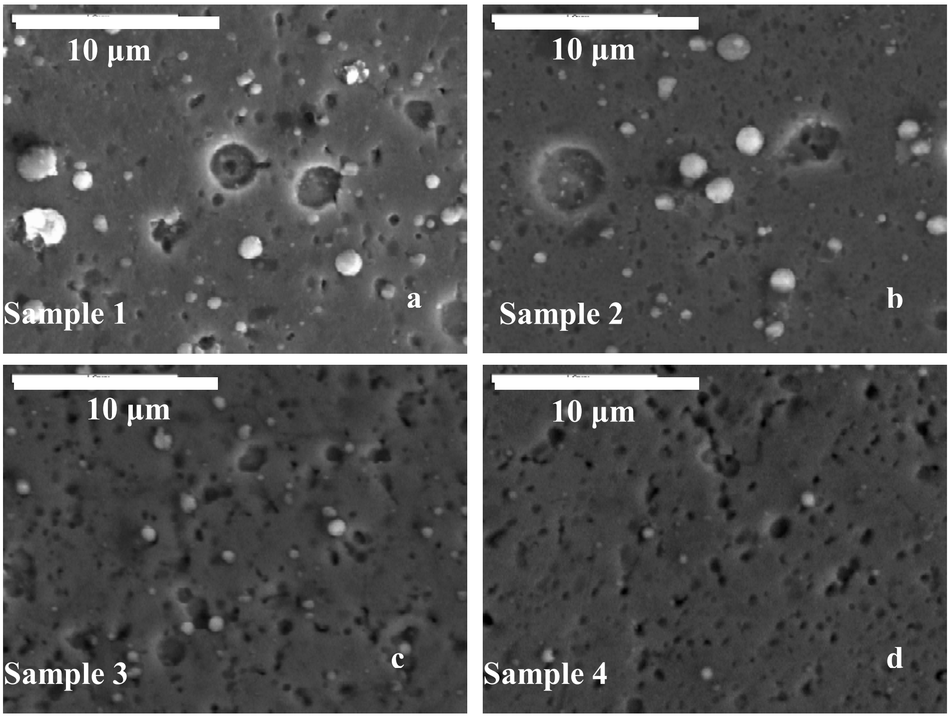


Fig. 8. Plain view SEM micrographs of the surfaces of samples 1-4

Plain view TEM observation of sample 1 revealed mainly the presence of stoichiometric TiN (fig.9b). From the dark field TEM micrograph of fig. 9a the average grain size was measured to be close to 150nm.

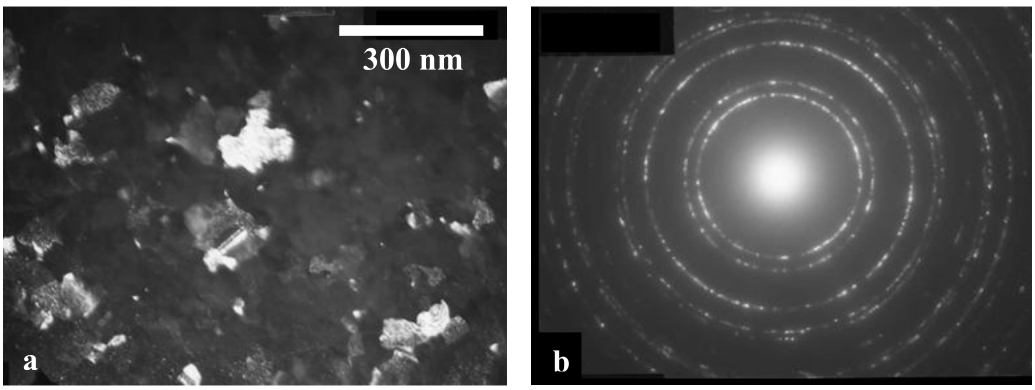
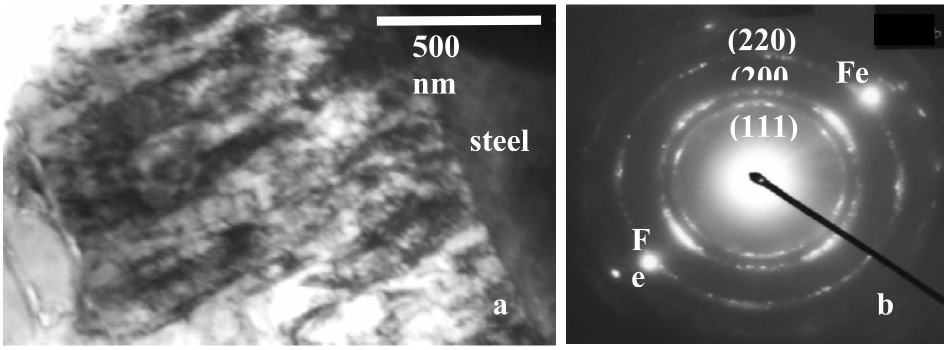


Fig. 9. TEM plain view micrographs and corresponding ED patterns of the normal (a, b) and the damaged area (c, d) of the coating.

Cross sectional examination of sample 1 revealed the columnar growth mode. In the ED pattern taken from an area close to the interface (fig.10b), TiN rings are present together with Fe spots coming from the substrate. As it is seen a preferential growth of the TiN grains is observed, following the Fe grain orientation. There are also several areas which contain non stoichiometric

TiN compounds. In the ED pattern taken from such an area (fig.10c), the spots are not laid on the stoichiometric TiN rings, indicating grains with different stoichiometry ranging from $TiN_{0.98}$ to $TiN_{0.76}$. This is clearly seen in the (200) spots which are placed inside the two enlightened rings.



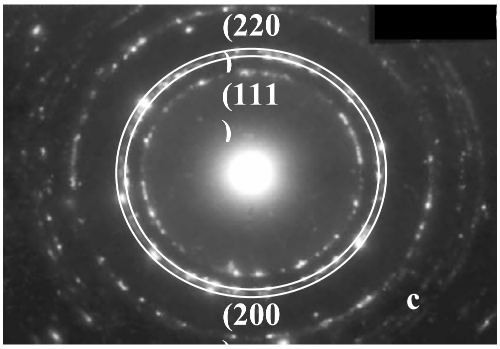
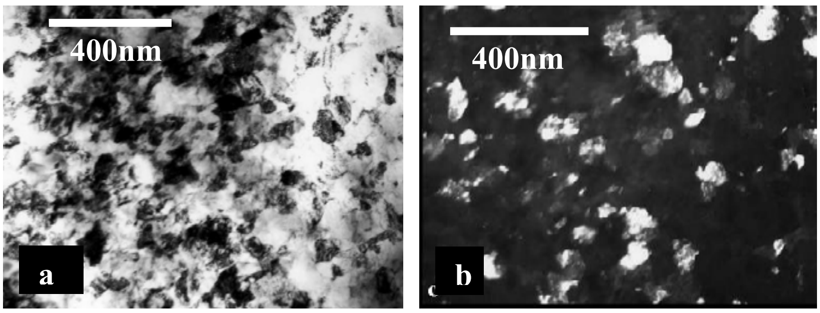


Fig. 10. Bright field TEM micrograph of the cross-section of sample 1 (a), ED pattern taken from an area close to the interface (b) and ED pattern taken from an area containing non stoichiometric TiN (c).

Plain view TEM examination of sample 2 (fig.11) revealed in this case only the presence of stoichiometric TiN (fig. 11c). In this case the grain growth is not accomplished towards any preferable orientation and from the dark field TEM micrograph of figure 13b the average grain size was measured to be close to 120nm. Cross sectional TEM examination of sample 2 (fig. 12) revealed also in this case the columnar growth of the TiN grains.



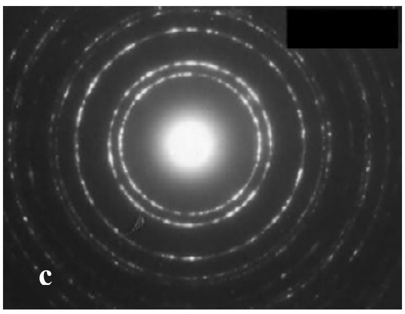


Fig. 11. Bright field (a), dark field (b) TEM micrograph from the plain view of sample 2 and the corresponding ED pattern (c).

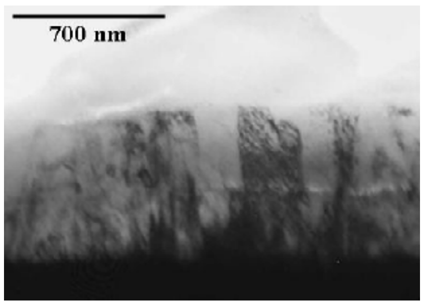


Fig. 12. Bright field (a) and dark field (b) TEM micrograph of the cross-section of sample 2.

Plain view examination of sample 3 (fig.13) revealed that in this case much smaller grains of the coating are formed. This concluded from the fact that the spots are small and numerous forming almost completed rings (fig. 13c). This remark is in agreement with the average grain size measured on the dark field TEM micrograph (fig.13b) which is 90nm. The brighter area in the (220) ring, as well as their six fold symmetry, reveal the preferential orientation of the TiN grains having their [111] direction parallel to the growth direction.

From the cross sectional TEM examination of sample 3, it was found that the TiN grains grow randomly near the substrate at the first steps of the growth procedure and then form columnar formations, further from the interface (fig.14a). The ED pattern, taken from the profile of sample 3 (fig. 14b), reveal the compositional homogeneity of the film consisting only of pure TiN.

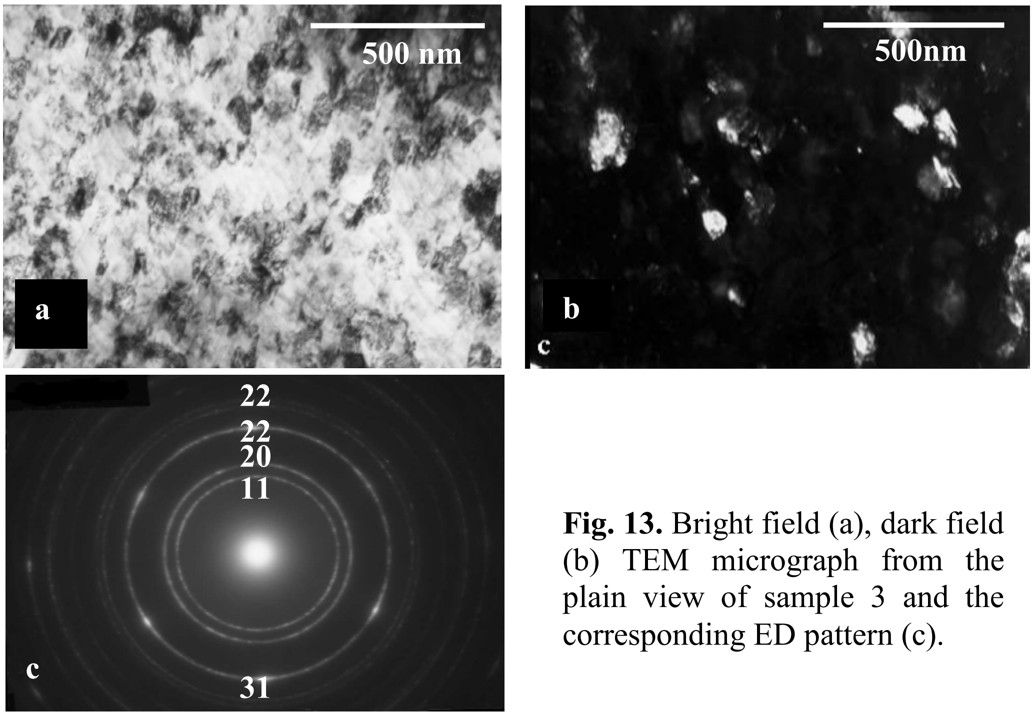


Fig. 13. Bright field (a), dark field (b) TEM micrograph from the plain view of sample 3 and the corresponding ED pattern (c).

Plain view examination of sample 4 (fig.15) revealed the formation of larger grains in comparison with the previous samples. The average grain size measured on the dark field TEM micrograph (fig.15b) which is 180 nm. Cross sectional examination of sample 4, confirm also in this case the columnar growth mode of the TiN coating.

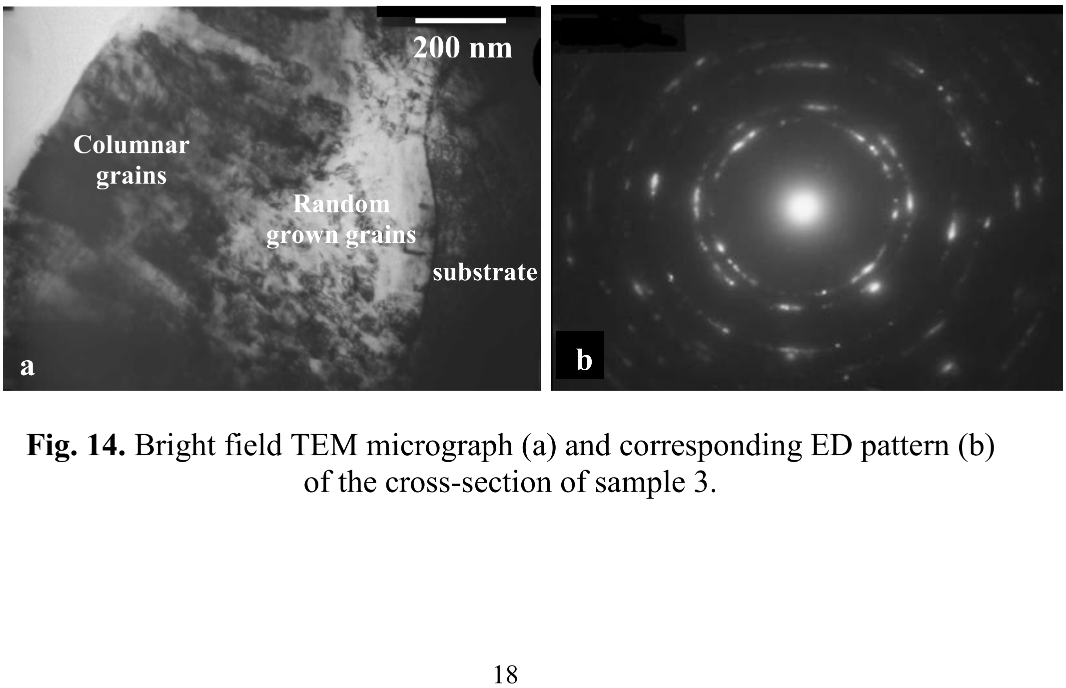


Fig. 14. Bright field TEM micrograph (a) and corresponding ED pattern (b) of the cross-section of sample 3.

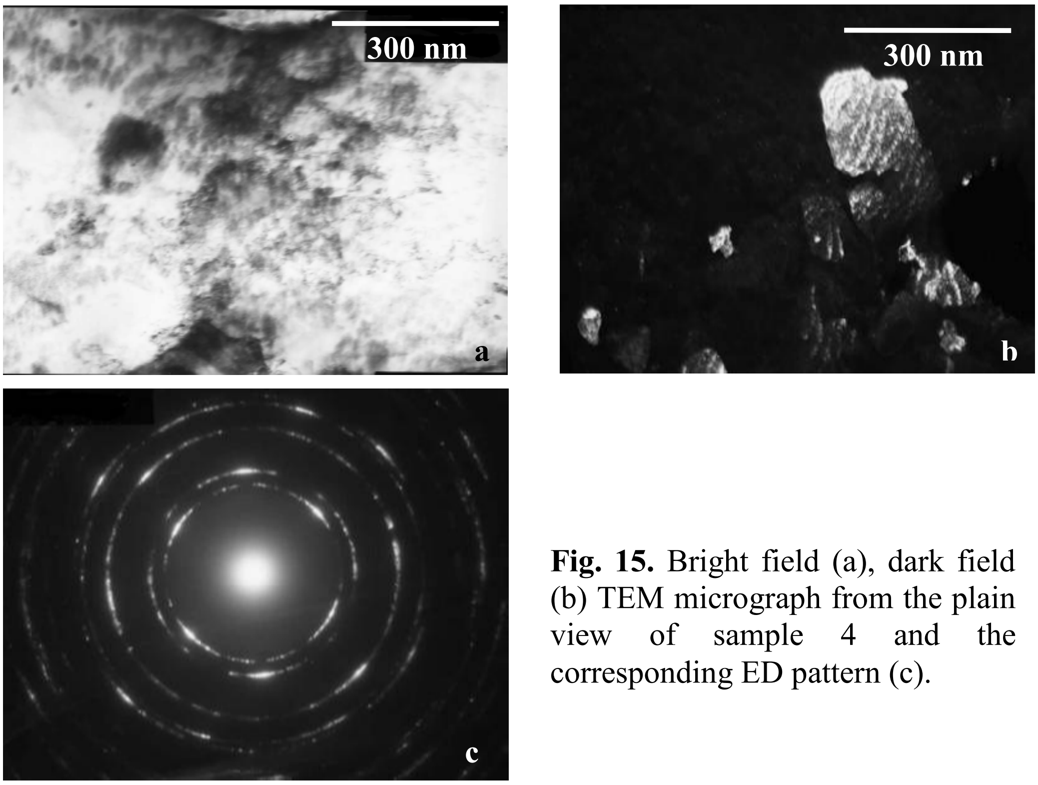


Fig. 15. Bright field (a), dark field (b) TEM micrograph from the plain view of sample 4 and the corresponding ED pattern (c).

Plain view examination of sample 5 (fig.16a) revealed that in this case grains with average size 100 nm are formed. From the corresponding ED pattern (fig. 16b) only stoichiometric TiN was found. The main feature of the cross sectional examination of the same sample is the columnar growth which is dominant in all samples.

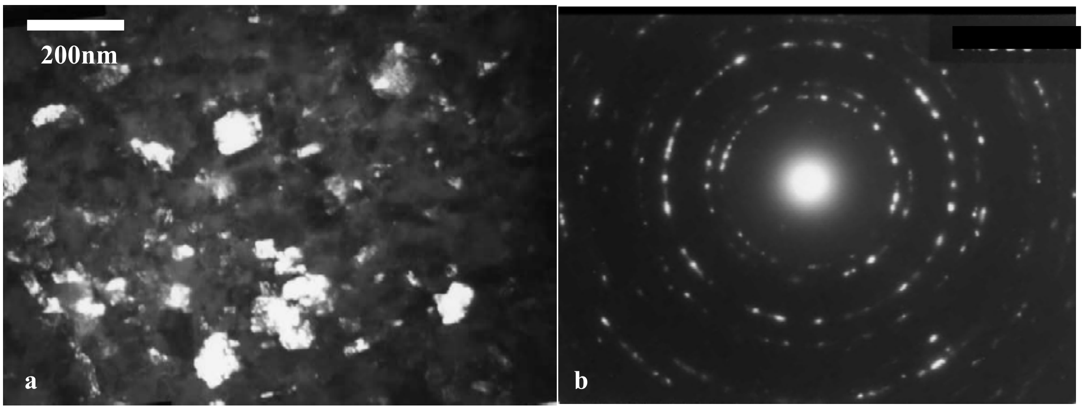


Fig. 16 - Dark field (a), TEM micrograph from the plain view of sample 5 and the corresponding ED pattern (b).

Conclusions

From this work the following conclusions can be drawn concerning the influence of the growth conditions on the microstructure of the coating. The quality of the TiN coatings it was found to ameliorate by increasing the N_2 flow increases in the vacuum chamber as the presence of TiN droplets becomes weaker. The as-coated tools have better mechanical performance because there is very little elimination of the coating due to the droplet cracking and so the tool maintains its surficial hardness. The growth of the coating follows the columnar mode. In the case where smallest TiN are grown (sample 2) they are also orientated towards [111] direction which provides supplementary hardness to the coating [23]. It was also found that the presence of Ar in the vacuum chamber during the coating procedure, lead to small deviations from the exact TiN stoichiometry near the interface areas of the coating (sample 1). Also the deposition temperature affects only the grain size of TiN as it increases with the temperature's rise. The thickness of the coating do not seem to be affected seriously from the temperature as it remains between 0.7-1μm for all the samples deposited at equal deposition times.

These measurable results like the grain size and the coating thickness in connection with the deposition temperature are also summarized in table II

Table II. The grain size and the coating thickness in connection with the deposition temperature for all the studied samples

Sample	Deposition Temperature (^{o}C)	Grain size (nm)	Coating Thickness (μm)
1	290	150	1.05
2	290	90	0.70
3	240	120	0.84
4	305	180	0.84
5	260	100	1.05

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Investigation on the TiN/Stainless Steel Interface Obtained by Cathodic Arc Deposition

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Keywords: TiN, hard coatings, microhardness, XPS analysis.

Abstract. TiN films are deposited on stainless steel substrates using cathodic arc deposition technology in different ambient gases. Coatings with a good reproducible thickness of 2 μm are obtained. The measured composite microhardness is in the interval 17 – 24 GPa (substrate hardness of 4 GPa) and depends on the deposition conditions. XPS depth analysis of the film and the TiN/SS interface is carried out to elucidate the influence of Ar in the reactive gas on the coating microhardness. The XP spectra and element distribution in the depth and at the TiN/SS interface reveal that Ar addition to the reactive gas hinders titanium oxides formation in the grown film. The latter could decrease the coating microhardness.

I. Introduction

Hard coatings based on transition metal nitrides and carbides are widely used for material protection against wear, abrasion and corrosion [1-4]. Because of their remarkable properties such as high microhardness, chemical inertness, high wear and abrasion resistance, these coatings have wide application in industry (cutting tools, dies, drills), medicine (instruments, implants, prosthesis), and as decorative tools. Among these coatings, TiN is an important material in advance surface protective coating area for steel [5]. Studies on TiN film properties have solved significant problems, such as the reduction of the usefulness of the TiN films for corrosion resistance coatings and for diffusion barriers in the films [6, 7]. Their main applications are in the machine industry as refractive materials, hard and wear resistant coatings on tools. Cathodic arc deposition (CAD) is the most used technique for obtaining hard and wear resistant TiN coatings [8].

TiN coatings are widely studied regarding their properties such as microhardness, surface morphology, adhesion and wear resistance. However, the mechanical properties of the films depend strongly on their chemical structure and composition. While the microstructure of the TiN films is extensively studied, little is known about the TiN/stainless steel (SS) interface chemistry depending on the deposition conditions. The latter are important due to their influence on the coating adhesion. The dependence of the technological regime on the film composition and TiN/SS interface obtained by CAD technique is investigated and discussed in this study.

II. Experimental procedure

TiN coatings were deposited on stainless steel, type SS420, which is used in industry for cutting tool producing. The samples were circles with a diameter of 45 mm and a thickness of 1 mm.

1. Surface treatment

The surface conditions before coating deposition strongly influlences the adhesion, wear and corrosion resistance of the film. Therefore, special attention was paid to preliminary surface cleaning. The samples were at first cleaned in standard organic solvents to remove all contaminations originating from the mechanical polishing procedure of the tools. A special technique, named electro-discharge polishing (EDP), was developed and applied to obtain a surface without contaminations and to reduce the surface roughness. The physico-chemical principle of EDP is presented in Fig. 1. The samples are immersed into an electrolyte, whose composition depends on the tool material. High voltage (300 V) is applied between the samples and the bath. Due to the high voltage, dissociation of the electrolyte begins and a vapour-gas area is formed around the samples. As a result, electro-discharge arises and the samples surface is etched. A surface with mirror brightness and a roughness $R_m \approx 0.02$ μm can be obtained. Detailed description of EDP technology and equipment is given in [9, 10].

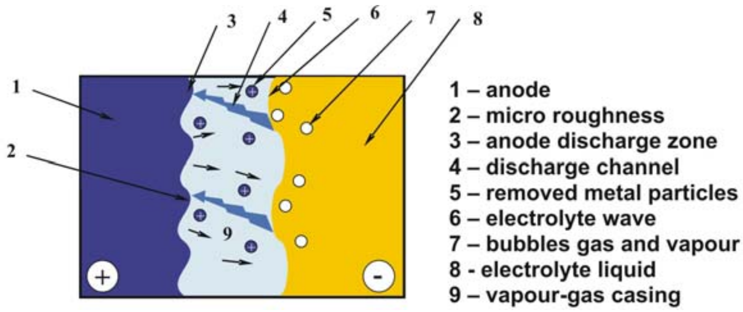

Fig. 1. Principal scheme of the EDP process.

2. Coating deposition

A schematic diagram of the cathodic arc deposition (CAD) system is presented in Fig. 2. The deposition part of the CAD system comprises two circular vertically-mounted arc sources (cathodes). Titanium targets with a diameter of 70 mm and a thickness of 55 mm are installed on them and used as a deposition material. The high purity of Ti targets (99.99 %) ensures the necessary quality of film deposition. The substrates are disposed on a planetary holder at a distance of 170 mm from the cathodes. The planetary holder is rotated continuously on its axis to provide a uniform film and to form the desired phase. To improve the coating adhesion and morphology, the substrates are heated to the desired temperature by two heaters mounted on the chamber walls. The temperature is maintained constant during the deposition procedure. Pumping and deposition processes are governed by a touch screen control panel on which a demo-scheme of the machine is also drawn.

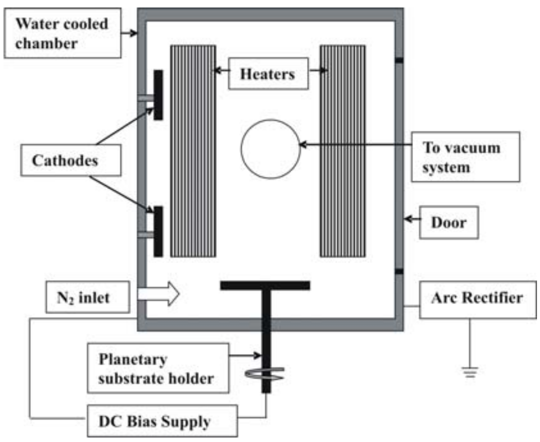

Fig. 2 A schematic diagram of the CAD system

On loading the chamber the system was evacuated to a pressure of $1x10^{-5}$ mbar. Then the substrates were based at a – 600 V potential and subjected to metal ion etching for 5 min using both Ti arc sources operating with a current of 90 A. This cleaning procedure enhanced the adhesion between coating and substrate. Before coating deposition, the substrates were heated up to the needed temperature whose value was determined by the substrate material. In the present study the temperature was chosen to be 290 ^{o}C because the substrates, tools respectively, were made of a tempered type SS420 stainless steel. The TiN coatings were reactively deposited using N_2 as a reactive gas. In several runs Ar was added to the reactive gas in order to check its effect on the coating properties. Both gas flows were precisely controlled by mass-flow controllers. The experiments were performed at a pressure ranging from $6x10^{-4}$ mbar to $6x10^{-3}$ mbar. During deposition, the substrates were biased with a DC power source (100 V) to induce proper ion bombardment on the growing surface. This assists in obtaining the desirable structure, grain size and film density. The values of all technological parameters described the experiments are given in table 1.

Table 1. Deposition parameters

Sample No.	Pressure [mbar]	N_2 [sccm]	Ar [sccm]	Dep.Temp. [°C]	Bias voltage [V]	Arc current [A]	Dep.time [min]
# TiN - 1	1.4×10^{-3}	300	0	290	100	90	90
# TiN - 2	4.1×10^{-3}	470	0	290	100	90	90
# TiN - 3	3.0×10^{-3}	300 (80%)	77 (20%)	290	100	90	90
# TiN - 4	6.0×10^{-3}	300 (73%)	112 (27%)	290	100	90	90

3. Coating characterization

The deposited coatings were characterized by measurement of thickness, microhardness and film composition.

The coating thickness was determined using Leitz Incident-light Microscope Interferometer which allowed measurements in the range 0.003÷30 μm. The method is based on two-beam interference arising out of a step between the deposited film and the substrate. The measurements were performed in monochromatic (λ=580 nm) and white light. The microhardness measurements were done on a Leitz microscope using Vicker's method with a load ranging from 20 to 200g. The film composition and the chemistry of the TiN/SS interface were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in a VG ESCALAB II system using AlK_α radiation with an energy of 1486.6.eV. The binding energies (BE) were determined with an accuracy of ±0.2 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The changes in composition and chemical surrounding in the depth of the films were determined on the basis of the areas and binding energies of Ti2p, N1s, O1s, C1s, Fe2p and Cr2p photoelectron peaks (after linear substraction of the background) and Scofield's photoionization cross-sections. The depth profile was obtained by ion etching of the film with 3 keV Ar^+ ions and a current density of 10 μA/cm^2.

II. Results and discussion

The measured thickness and microhardness of the TiN films studied are listed in table 2. The same parameters of SS420 stainless steel substrates are presented for comparison. It was established that the developed technology allowed good reproducibility of the film thickness. The latter depended mainly on the deposition time with a fixed cathode configuration. Thicknesses of 2 μm (±0.1 nm) were measured for all TiN films deposited for 60 min, irrespective of the reactive gas composition, gas flow and pressure during deposition.

Table 2. Parameters of SS420 substrates and TiN coatings.

Parameter	Sample No.				
	SS 420	**# TiN - 1**	**# TiN - 2**	**# TiN - 3**	**# TiN - 4**
Thickness, d [μm]	1000	2	2	2	2
Hardness, h [GPa]	4	17	16	20	24

The presented composite microhardness is determined by extrapolation of the experimental data measured with a load varying from 20 to 200 g. The extrapolation has been done using Bull's model [11] with a correlation coefficient 0.998, which is an indication of appropriately selected parameters. It is obvious that the microhardness increases 4 to 7.5 times as a result of the TiN coating deposition. The results from the experiments show that the reactive gas composition has a significant effect on the microhardness of the coatings. It is found that the presence of Ar in the reactive gas increases the coating hardness. A small increase in Ar amount results in an increase of the hardness (samples #TiN-3 and #TiN-4). This result could not be simply explained, moreover that the TiN films deposited in an N_2+Ar gas mixture have a rougher surface than the ones deposited in N_2 only. For better understanding of the results obtained, XPS analysis on two samples with TiN coatings deposited in N_2 and N_2+Ar atmospheres was performed.

Figs. 3 and 4 present Ti2p, N1s, O1s, and C1s photoelectron spectra with different sputtering time, for the coatings #TiN-1 and #TiN-3 deposited in N_2 and N_2+Ar, respectively.

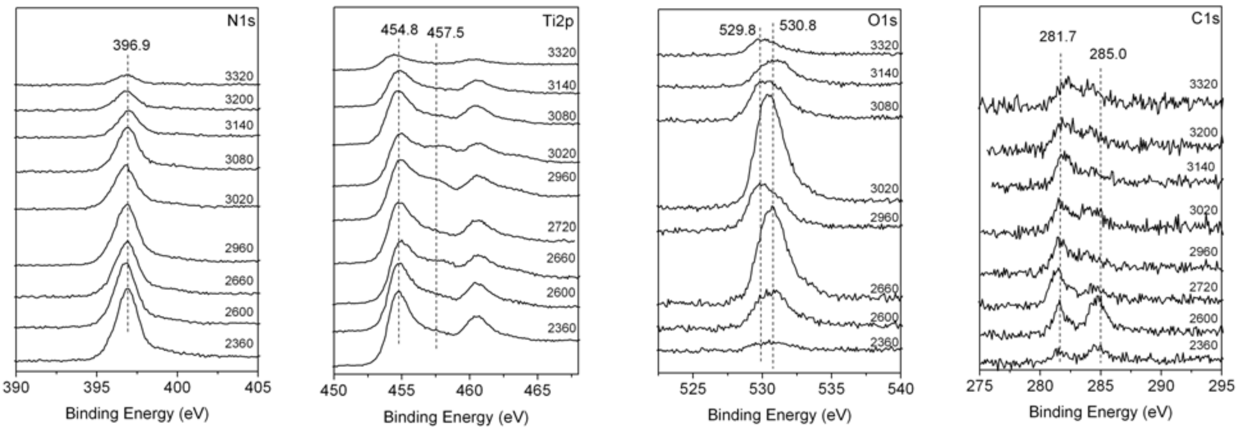

Fig. 3. Ti2p, N1s, O1s and C1s photoelectron spectra obtained for different sputtering times on sample #TiN-1 (deposited in N_2).

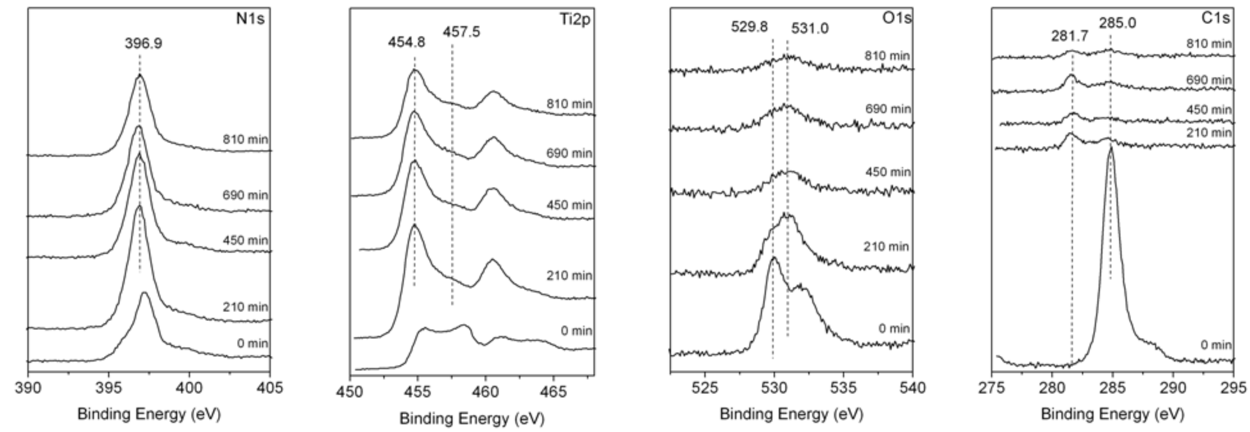

Fig. 4. Ti2p, N1s, O1s and C1s photoelectron spectra obtained for different sputtering times on the sample #TiN-3 (deposited in N_2+Ar).

The binding energies of Ti2p (454.8 eV) and N1s (396.9 eV) peaks determined on both samples are close to the ones reported for TiN [12]. In both C1s spectra a peak shoulder at ~282.0 eV was observed, which is typical of carbon in a carbide state. This suggests that during the deposition process, TiC is also formed. The presence of relatively intensive O1s peak at 530.3 eV is registered on the sample #TiN – 1. Similarly, in most spectra a shoulder of the Ti2p peak at ~457.5 eV is detected. Its intensity correlates well with the intensity of the O1s peak observed during sputtering for 2770^{th} to 3200^{th} minutes. This fact as well as the measured binding energies of the O1s peak and the shoulder of the Ti2p peak (characteristic of Ti^{3+}) pre-supposes the presence of a Ti_2O_3 phase in the layer. O1s (at 530.4 eV) and Ti2p (at ~457.5 eV) peaks are also observed with the sample #TiN – 3. However, they are less intense as compared to the ones for sample #TiN-1. The shoulder of the O1s peak registered at 531.0 eV may be due to the adsorption of hydroxyl groups present in the residuum gases in the vacuum chamber. This follows from the fact that the shoulder at 531.0 eV appears at large sputtering time when the bulk of the film has been reached.

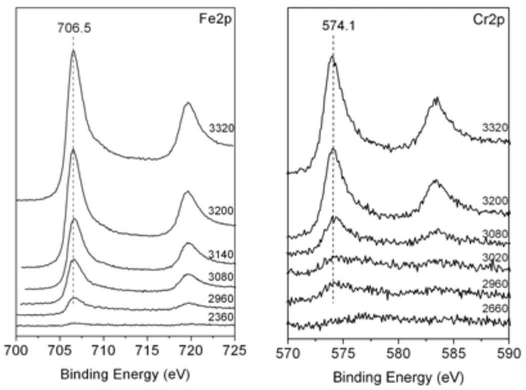

Fig. 5. Fe2p and Cr2p photoelectron spectra obtained for different sputtering times on the sample #TiN-1 (deposited in N_2).

The measured photoelectron spectra of both samples show that the amount of the Ti_2O_3 oxide phase in the coating deposited in a N_2+Ar atmosphere is less than that in the coating deposited in N_2.

Fig. 5 presents the Fe2p and Cr2p photoelectron spectra of the sample #TiN – 1. It is seen that these peaks are registered after sputtering for more than 2300 minutes, which is very close to the TiN/SS interface. Binding energies of 706.5 eV and 574.1 eV have been measured for the Fe2p$_{3/2}$ and Cr2p$_{3/2}$ peaks, respectively. This result presupposes that the above elements are in the metal state at the TiN/SS interface.

Based on the spectra measured, the XPS depth composition of the coatings deposited in N_2 (sample #TiN -1) and N_2+Ar (sample #TiN -3) atmosphere was obtained. The element distribution in the coating layers and at the interface for the sample #TiN -1 (prepared in N_2 atmosphere) is shown in Fig. 6. From the element distribution in the depth of the TiN layer (Fig. 6a) it could be supposed that the stoichiometry of the coating differs from the theoretical value for the titanium nitride. In the interval from 0 to 2700 min of sputtering the nitrogen concentration exceeds the concentration of titanium. During sputtering for 2770 to 3200 min, a strong increase in oxygen concentration is observed, which correlates with the shoulder increase of the Ti2p peak (at ~457.5.eV) and is typical of the Ti_2O_3 oxide phase. Fig. 6b presents the element distribution in the region of the coating near the TiN/SS interface as well as at the very interface. The interface with the stainless steel substrate is nearly abrupt. The presence of N and Ti is observed even at relatively high concentrations of iron, which could be explained by diffusion of some Ti and N into the stainless steel surface during deposition. This diffusion is most probably due to the high ion energy.

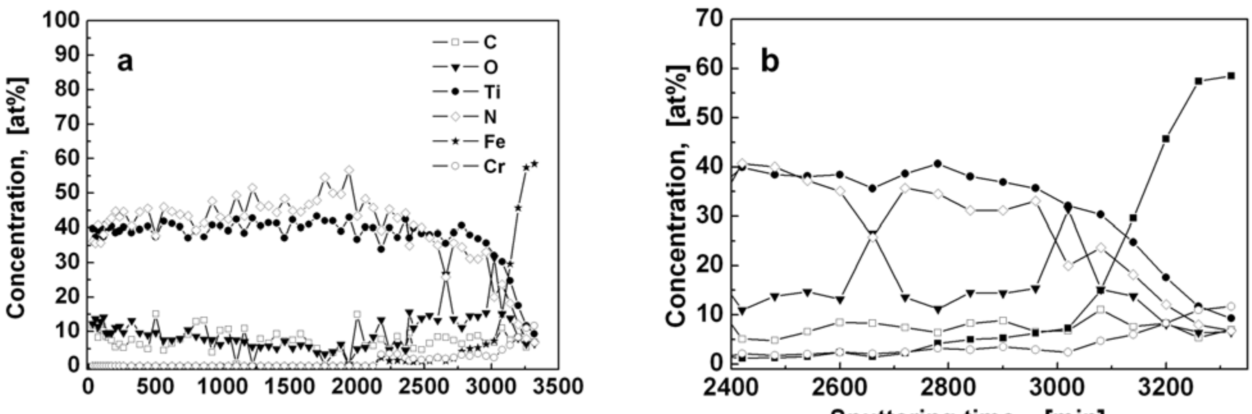

Fig. 6. XPS depth profile of the element distribution for the sample # TiN -1:
a) whole coating thickness; b) interface area.

XPS depth profiles of element distribution after 800 min sputtering for both samples are compared in Fig. 7. This time corresponds to etching of 1/3 of the coating below the surface. It is enough to provide

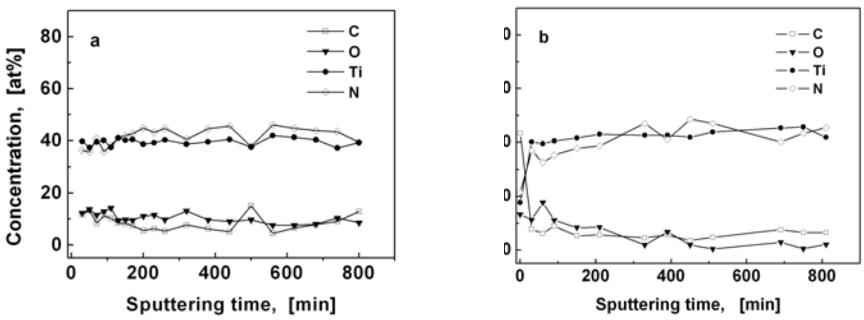

Fig. 7. XPS depth profile of the element distribution after 800 min of sputtering : a) sample # TiN -1; b) sample # TiN -3.

information about the film composition which could be responsible for the coating microhardness. The XPS depth profile of the sample #TiN – 3 reveals that near the surface the nitrogen concentration is lower than that of titanium, whereas in the film depth both concentrations become commensurable. The oxygen concentration in the coating is reduced significantly. A small amount of oxygen is detected in the surface region only, while in the depth it is practically absent.

Conclusion

The XPS depth analysis of TiN coatings deposited in different regimes has revealed that the film composition depend on the reactive ambient gas. Deposition in N_2 atmosphere even at pressure as high as $1.4x10^{-3}$ mbar (300 sccm gas flow) does not prevent oxygen contamination from the residual gas in the vacuum chamber. Due to the high affinity of Ti towards the oxygen, a titanium oxide phase (Ti_2O_3) is formed during the film growth. Its amount is higher (~15%) at the interface and in the region near it. In the upper layers, the oxygen amount decreases to ~10% and remains almost constant in the rest of the film. On contrary, addition of a small Ar amount (~20%) to the reactive gas prevents oxide formation during the growth process. XPS analysis does not show essential difference of the Ti/N ratio in the samples studied despite the different deposition medium. This result allows assuming that the presence of titanium oxides in the TiN layer is the reason for the lowered microhardness of the coating. We suppose that the observed difference in the microhardness of the samples prepared in N_2 and N_2+Ar atmosphere is due to the Ti_2O_3 inclusions formed during the deposition process.

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New Electro Discharge Polishing Equipment

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Keywords: polishing, electrolyte discharge, equipment, thermoregulation, protection

Abstract: Electro discharge polishing is a new efficient method for modification of surface of constructive materials by high energetic electromagnetic fields [1]. Especially interesting for applications is modification of stainless steel, leading to polishing. The objective of this work is to design and construct equipment for electro discharge polishing of details of stainless steel. The equipment is composed of thermostatic tank, electronic block Power Supply and electronic block Control. By reasons of using high voltages (up to 350V) and large current (up to 100A), special attention is noticed of the protection, that ensure the safe and non-damage work. Regardless of the fact that tank is thermostatic with water mantle it is used special thermoregulator for insurance necessary work temperature with tolerance ±0.5°C.

Introduction

Polishing is a process of creating a smooth and shiny surface by using rubbing or a chemical action in objective to enhance the quality of the surface. In dependence of using and purpose, which have to be achieved, the polishing is mechanical and chemical. The mechanical polishing is done by rubbing the surface most often with abrasive material. The chemical polishing, called also anodic, is based on chemical reaction in electrolyte environment, initialized of passing electric current. This polishing is separated on two kinds: electrochemical and electrolyte discharge.

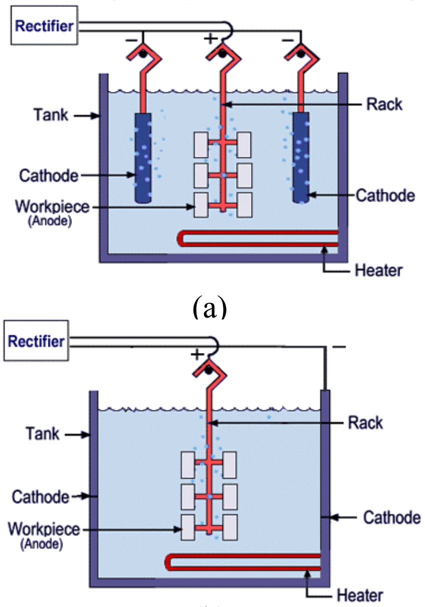

Fig. 1. Scheme of the systems for: a) electrochemical and b) electro discharge polishing

Electrolyte discharge polishing is a new method for processing the surface of details developed in last years. Its main advantage is allowing simultaneous qualitative machining of the whole surface of the detail [1]. In electro discharge polishing (EDP), like electrochemical, leaks chemical reaction between the processed material and the electrolyte. The essential difference in EDP process is the role of the tank, voltage and temperature values. These differences in the nature of the process give rise to corresponding discrepancy in the constructive part of the equipment.

This paper presents the developed new equipment for EDP in comparison to the electrical chemical polishing. In electrochemical polishing (Fig.1a) the system is composed of tank, electrolyte, cathode and anode on which anode the polishing details are hanged. In this case the tank is only vessel for the electrolyte, in which one is done the process of polishing. From a rectifier is applied voltage and between the anode and cathode pass current. Under its action is done electrolyte dissociation and goes electrochemical reaction. As a result of it from the surface of the detail has been taken ions and this is the way of accomplishing the polishing. To enhance the process the electrolyte is heated by heater. While in the EDP (Fig.1b) the tank become to be a cathode of the system and the process run between it and the detail, which is the anode. So the whole amount of the electrolyte becomes a shell for the processed detail in result of it runs polishing of the entire surface. It could be summarized that both polishing processes are anodic, accomplished in heated electrolyte. But while the electrochemical is done on voltages in range 6÷25V and temperatures of the electrolyte in range 20÷70ºC (the values depends from the type metal which has been processed), for realizing of gas shell in EDP is needed voltage in range of 80V to 380V and temperature of the electrolyte 80÷900ºC. This lay down definite terms to the equipment for this type of polishing. These terms are in two directions: sustain stable process in the time characterized with constantly voltage and temperature, and protection of the equipment and the operator working on it.

Development of new equipment for electro discharge polishing of stainless steel Electro discharge polishing is a new method, which has been demonstrated already its advantages to electrochemical polishing and which one is forthcoming to obtain wide dissemination. That's why developing and building of proper equipment represents research interest [2]. The exhibit in this paper equipment is improved variant of basic demo model. It is added new elements in the field of thermal stabilization, management and indication of the process and protection.

1. Description of the equipment

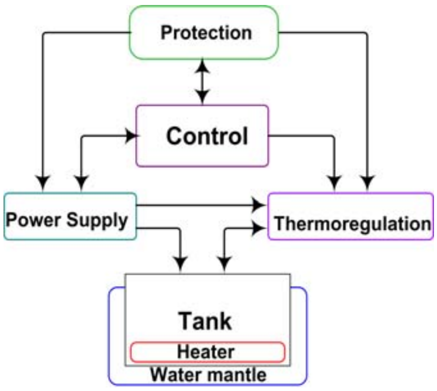

Fig.2. Block scheme of electrolyte discharge polishing

On Fig.2 is shown the block scheme of the equipment for EDP, the connections and its directions. *Power supply* executes two functions: (1) provide power supply for all devices in the equipment and (2) ensure stable technological voltage, needed for the process of EDP. *Control* contains the managing apparatuses of the equipment. The control is automatic (by default) or manual. In automatic rate it has be given the sequence of work and it has be track the process of thermal regulation. *Thermoregulation* is realized on three stages: reading the state of the object, elaboration of influence and exert influence on the object. The tank could be examined like an object of regulation. *Heater elements* are made of cupper coil over ceramic base, electrically isolated from the tank, but with excellent thermal connection with it. The water mantle envelope the tank and managing of the cooling is done by electromagnetic valve. *The Protection* block ensures conditions for safety work of the operator and the equipment. The original parts of the structure of the equipment are the blocks for thermoregulation and protection so they would be observed in details.

1.1. Thermal regulation

One of the most important parameters of EDP is the temperature. For achievement of surface with high quality (little roughness, brightness and etc.) it is demand continuous thermal stabilization of the electrolyte. The process of thermostabilization could be observed like compound of two phases: preparation and real polishing. In preparation the electrolyte has to be heated to definite work temperature that has to be kept constantly in time. By Automatic Regulator(AR) it is been controlled heater element like separated in way of heat power is detected by thermal sensor. The sensors are selected on base measured temperature range and wanted accuracy. On Fig.3 is shown the system for automatic regulation of the temperature [3]. The input of the AR is feed with information for the temperature of the object and the AR elaborate proper on value influence which could be current or voltage. This is realized by the following way: with thermoresistance it is read the heating of the electrolyte. In the MD the read information is processed and set in mode, usable from the scheme(linearization, amplifying and discretization). In CD the received from MD value in mode of current or voltage is comparing with this value that is set in SD. The result of comparinggoes to the input of ATD, where is made the transforming and by ED is applying proper influence to the object, expressed in starting the heaters if temperature is decreased or stopping them if temperature is increased over the set.

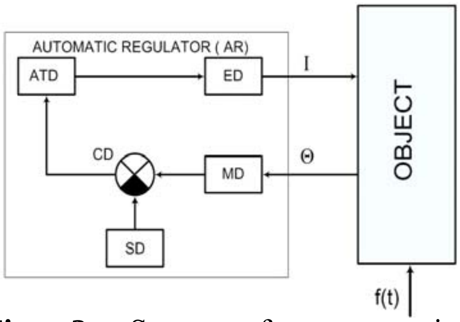

Fig. 3. System for automatic regulation MD – measuring device; CD – comparing device; SD – setting device; ATD – amplifying - transforming device; ED – executive device; the quantity f(t) represents the dissipation heat in the surroundings, thermal losses.

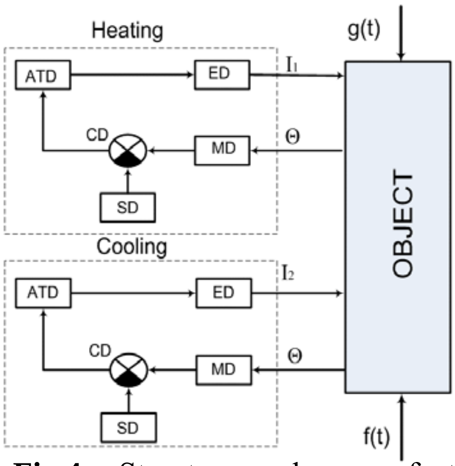

Fig.4. Structure scheme of the regulation of heating and cooling during the process of polishing.

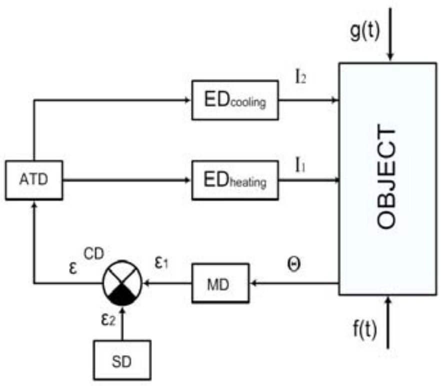

Fig.5. Structure scheme of regulator, controlling two processes – heating and cooling; ε - difference between set (ε_2) and measured (ε_1) value of temperature.

The process of EDP is exothermal so in the bulk of electrolyte. is dissociating an extra quantity heat g(t). The process of dissociating heat in the surrounding the tank area f(t) is much slower than the process of extra heating g(t). That leads to increasing the temperature of the electrolyte and then to changing the technological regime. This lay down induction of system for cooling (Fig.5). With that realization the system is composed of two automatic regulators like part of their structures are same – temperature sensors, measuring devices (MD), setting (SD) and comparing devices (MD). As a matter of principle these devices are implementing same actions and the regulated quantity is only one – the temperature. That permits to use one thermoregulator with shown on Fig.5 structure. In the amplifying – transforming device (ATD) is read the sign of the quantity ε, which performs the difference between the set and the measured value ($\varepsilon = \varepsilon_2 - \varepsilon_1$). In result it is feed with managing signal the $ED_{heating}$ or the $ED_{cooling}$ where will be produced managing influences I_1 and I_2. On this way only with adding one device to automatic regulator it can be controlled two different processes, heating and cooling.

In the created equipment for EDP it is used specially developed microprocessor thermoregulator as executive devices are taken away of its structure in purpose to its miniaturizing and optimizing. Thus it obtains multivariable of the system for thermal regulation. The accuracy of regulating the temperature ±0.5°C, as it is managed simultaneously the both processes

The microprocessor regulator offers some kinds of outputs - current, voltage, relay, as it give the possibility for Pulse – Width Modulation (PWM), when this is needed from the management. The choice of kind output depends from executive device. And with bringed out on panel indication it is given the current temperature of the electrolyte, set temperature and which executive device in the present moment is working.

1.2.Executive devices

Executive devices are part of the thermal regulation, but they are not in the structure of the regulator. The controlling influences of the regulator are with little values voltages and currents. They had to commutate much bigger currents and voltages. The electronic base nowadays offers a decision compounding in one classical techniques of management with new approach by using Solid State Relays (SSR). They are devices from relay type but offer bigger reliability than classical relays, galvanic or optical split and compactness in proportions. Moreover their sensitivity is much bigger than electromagnetic relays when the output values of the quantity are same. The main type used SSR are photo-isolated, because they are much easier realizable than transformer one and dissipated power is lesser. Since SSR control only heaters it is needed to have a device, commutating the water. Such device is electromagnetic valve (EMV). It is electromechanical device of relay type which opens itself when receive proper managing influence and let through the water flow in water mantle of the tank and it is done the cooling process. This valve allows work in pulse mode like the frequency of commutation do not create disturbance for normal functioning. That permit to be managed by PWM if this is necessary.

2. Protection

Because of the specific of the process EDP, namely voltages up to 380V, currents up to 90A and temperatures about 90ºC, it has to be taken increased measures for safety. These measures are with object to protect the operator and to ensure safe work of the equipment. Conditionally the protection could be separated on electrical and mechanical, but it has to be known that they work connected. The electrical protection is connected mainly with technological currents and voltages, the heating of the elements in the process of work. It is composed of: *automatic circuit-breakers*, *circuit closers, emergency stop, limiting switches, fans and thermal circuit-breaker*. The automatic circuit-breakers ensure break of the circuit at overloading or at disturbance in the supplying network. Because of the specific of the process of EDP it is used DC automatic circuit-breaker. It is controlled by AC voltage, but commutates DC voltage. On this way the high tension apparatuses is protected from without a break switching in the process of work. So only this breaker switches and commutates the high voltage feed to the tank. When a detail is polishing, the breaker turns on and when is needed other operation which is no need of technological voltage in working area it turns off. The emergency stop is a obligatory element of the protection, it stops the high voltage totally – its pressing breaks the circuit for supplying of the equipment. The limiting switches are electromechanical devices which provide upper and lower limit of motion of the mechanism for plunging the processed details. The lower limit does not allow the detail to touch the bottom of the tank and to make short circuit. The upper limits the motion from above. The fans made the cooling of high tension part of the equipment by force convection. They assist the work of sinks in the Power supply block. They are very important when the equipment is high power. The thermal-breaker ensures breaking the circuit of the transformer when it is reached determinate temperature inside the coils. This temperature is reached when the dissociated heat power could not be dissipate in the surround area. Mechanical defense is designed for protecting the operator on the machine from side effects of the process – like vapors. Also protect of accessing the opened current providing parts of the equipment.

Summary

Electrolyte discharge polishing is a comparatively new method for processing the surface. In this paper is heard the developed new equipment for applying it. It is accented over the new and the improved elements prompted by the specific of the process. It is reached precise thermal regulation by microprocessor regulator with multi variable outputs, so in result of this the temperature of the electrolyte is kept constantly with accuracy ±0.5°C. It is developed a new scheme of executive devices based on SSR and pulsed EMV, which enable pulse rate of work and management through PWM. It is achieved improvement by using DC automatic circuit-breaker in view of working with high voltage up to 380V in aggressive environment (the electrolyte). Such created equipment provides unlimited continuance of work and stable in time parameters of the technological process which allows increasing the processing surface to 500 cm^2.

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Microhardness Measurement by Indentation of TiN, Ti(CN), ZrN, (ZrTi)N Hard Coatings

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Keywords: Coating hardness, work-of-indentation hardness model, composite hardness, intrinsic hardness, non-linear curve fitting.

Abstract. Available indentation techniques for measuring hardness of thin-layered coatings on softer substrates have been assessed for usability in routine characterization needed in thin film deposition development. A convenient express procedure to extract thickness-independent hardness from a series of indentation probing has been applied. The method is based on a popular work-of-indentation analytical model that can provide reasonable estimates of layered material intrinsic hardness obtained from composite hardness data (i.e. with contributions from both the coating and substrate) as a function of penetration depth. Extrapolated non-linear curve fitting of experimental data points to zero penetration provides the estimate. The attained accuracy is assessed in terms of measurement errors and validity limits of the deformation mode models.

1. Introduction.

Development of technology is a continuous process of reactor design modification, physical and chemical reaction mechanisms study and characterisation of the resultant layers driven by the developer's ingenuity based on active feedback between changes in the product properties and technological conditions. Thus to progress in our objective of producing hard and superhard coatings for industrial applications, we need to have reliable estimations of the structure, hardness, adhesion and wear and corrosion resistance of thin film coatings on various, usually softer substrates. In the present paper we are concerned with unambiguously assessing the coating hardness from a series of laboratory indentation tests. Veprek [1] has pointed out the importance of correctly measuring the hardness of superhard coatings and explained that only load-invariant values obtained at typical maximum applied load of 30 to 150 mN and indentation depth of greater of equal to 0.3 μm should be reported. As an empirical rule it has been established that in order to measure the hardness of hard coatings on softer substrate correctly, the maximum indentation depth must not exceed 10% of the coating thickness because above that limit noticeable plastic deformation in the softer substrate occurs. Lichinchi et al. [2] have proven the existence of such a limit (at 15% of film thickness) by means of finite element modeling of the indentation process in TiN coating on high-speed steel. More recent indentation simulations with the finite element method modeling in the superhard range (hardness > 40 GPa) by He and Veprek [3] revealed that because of the higher strength of such coatings, the maximum indentation depth should not exceed about 5% of the coating thickness in order to avoid plastic deformation in the substrate. Then for hard coating films a so-called indentation size effect occurs where the apparent measured hardness increases as the indentation area is decreased. Its nature is complicated as has been discussed by Bull [4] and makes extracting bulk hardness of the coating in question virtually unreliable in nanoindentation testing at very low loads (< 30 mN).

2. Experimental

All coatings tested were deposited by cathodic arc deposition on stainless or stainless steel substrates undergone either standard electrochemical or electrodischarge surface polishing. Nitride films were grown at nitrogen partial pressures high enough to ensure the synthesis of the corresponding single metal nitride phase but excluding source cathode poisoning. Carbonitride films were grown using a mixture of methane−nitrogen and in some cases argon gas maintained at constant ratio by adjusting the corresponding flux by mass flow controllers. The metal component has always been supplied by the cathode arc. Figure 1 shows various coated parts in our CAD equipment.

Coating thickness was determined on concomitant single crystalline Si specimens placed near the coated parts in the chamber. The thickness was measured on a Leitz optical interference microscope where the height of a step formed via contact mask during deposition was determined from the shift in the interference pattern (obtained in an optical wedge) with an accuracy of ~ 30 nm. Due to variation in the slope and span of the step the effective error was increased to ~ 100 nm.

Hardness testing was performed on a standard Vickers microindenter LOMO with a square diamond pyramid of 136° apex angle. A series of increasing loads were applied starting from 40 g and going up to 220 g. Penetration depth and the corresponding composite hardness was calculated from the projected indentation diagonal using a simple geometric consideration. Each reported value has been averaged over 5 samplings.

3. The coating−substrate hardness model

The primary goal of this research was to obtain consistent numerical hardness that would be representative of the coating material and would exclude dependencies on film thickness and substrate or sublayer hardness using measured data from macro- and microindentation (since a nanoindenter was not available on routine basis). Among the analytical models describing the coating−substrate system reaction to indenter penetration only a few require a small number of fitting parameters or use directly measurable quantities to produce the composite hardness output as a function of the applied load in a range as wide as two, three or more orders of magnitude. Two such models meet our requirements of applicability and simplicity, namely Korsunsky et al. [5] and an extension of the latter by Tuck et al. [6], both developed at the University of Newcastle. They are based on the concept of the work-of-indentation and as such include contributions to composite measured hardness from various deforming mechanisms like coating fracture, delamination, plastic flow in both film and substrate and mixed failure modes when more than one mechanism may operate [4−6]. The first model presents the composite hardness as

$$H_c = H_s + \frac{H_f - H_s}{1 + k\beta^2}, \qquad (1)$$

where H_s is substrate intrinsic hardness, H_f is film intrinsic (bulk) hardness, β is the relative indentation depth, $\beta = h/t$, where h is the penetration and t is film thickness, and k is a dimensionless parameter characteristic of the coating/substrate pair and the operating deformation mechanism which remains constant over a number of orders of magnitude of relative indentation depths. This formula provides a symmetric smooth two-level transition curve if a logarithmic scale for β is used.

The exponent of β has been made variable in the second model thus achieving better analytical curve fitting to the experimental data points at the expense of increasing the number of fitted parameters by one. Physically exchanging the quadratic power dependence on β for a variable one reflects contributions from multi-mode deformation taking place simultaneously. Thus β_0 has the

$$H_c = H_s + \frac{H_f - H_s}{1+\left(\beta/\beta_0\right)^X}, \text{ where } k = \beta_0^{-X}. \tag{2}$$

meaning of a characteristic relative indentation depth where the composite hardness is reduced by one half the difference between the coating and substrate intrinsic (bulk) hardness [6]. Obviously this formula should represent a similar to equation (1) transition curve of adjustable steepness set by the exponent X [6].

4. Extracting the intrinsic coating hardness

The two work-of-indentation models were constructed to assess the hardness improvement introduced by the hard coating with regard to particular surface loading. Here we are concerned with the *inverse problem of extracting the bulk intrinsic hardness of a coating from a set of composite hardness data taken at different loads*. This set, as practice has shown, is often incomplete as microindentation alone cannot provide penetration in terms of relative indentation depth (RID) neither in the few hundredths to one tenth range, nor in the range 3 to 10 and higher, thus excluding the asymptotic convergence (seen on a logarithmically scaled abscissa plot) of the fitting curve to the intrinsic coating and substrate hardness.

The computer software to fit non-linearly a curve to a data point set operated as follows: an analytical (fitted) function (the composite hardness) of an independent variable (β) with *parameters* (β_0, H_f and the exponent X) *subject to determination* was the input and the output produced were the parameters in question. The program had the additional capability of drawing the curve once the fitting parameters had been computed.

The raw experimental data points for some single-layered coatings are presented in Figure 2 on linearly scaled penetration depth axis. The tendency is clear: with penetration decreasing the composite hardness increases but with no apparent clue as what the intrinsic film hardness would approach at zero load.

Fig. 1. Steel parts coated by Cathodic Arc Deposition at the Institute of Applied Physics with various hard coatings as indicated.

Figure 3 presents two composite hardness data sets taken from two coatings of the same TiN material on SS420 steel but of different thickness. A best fitting curve for these using equation (2) is plotted for both coatings. Both plots have the data points distributed asymmetrically along the fitting curves, more of them supporting the curve on the lower hardness region. Substrate hardness is 5.58 GPa in both cases.

Figure 4 presents a Zr(CN) coating on stainless steel where no data point for the substrate hardness exists. Apparently a fairly smooth and plausibly fitting curve exists with fitting parameters as indicated in the legend field.

Then Figure 5 presents a data set of composite hardness for a ZrN film on stainless steel substrate. All attempts to produce a reasonably well fitting curve failed with some of the parameters returned negative. This lacks physical sense, so the fitting curves were rejected and none has been drawn.

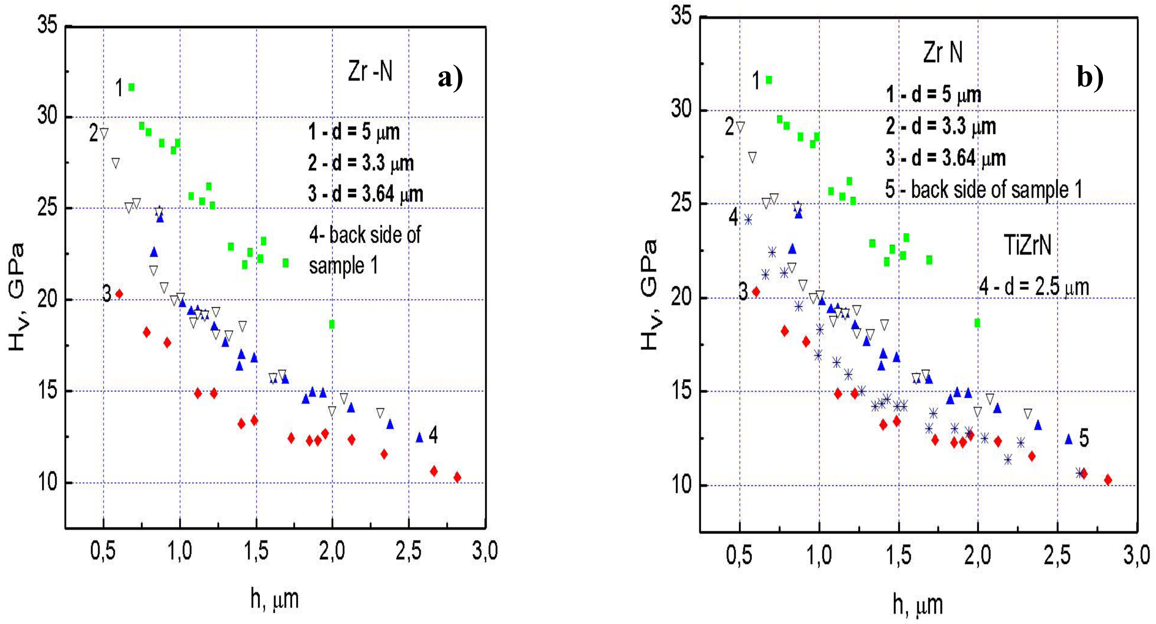

Figure 2. Composite hardness of ZrN coatings (a, left) and ZrN and (TiZr)N coatings (b, right) plotted as raw data on a linear penetration−hardness plot.

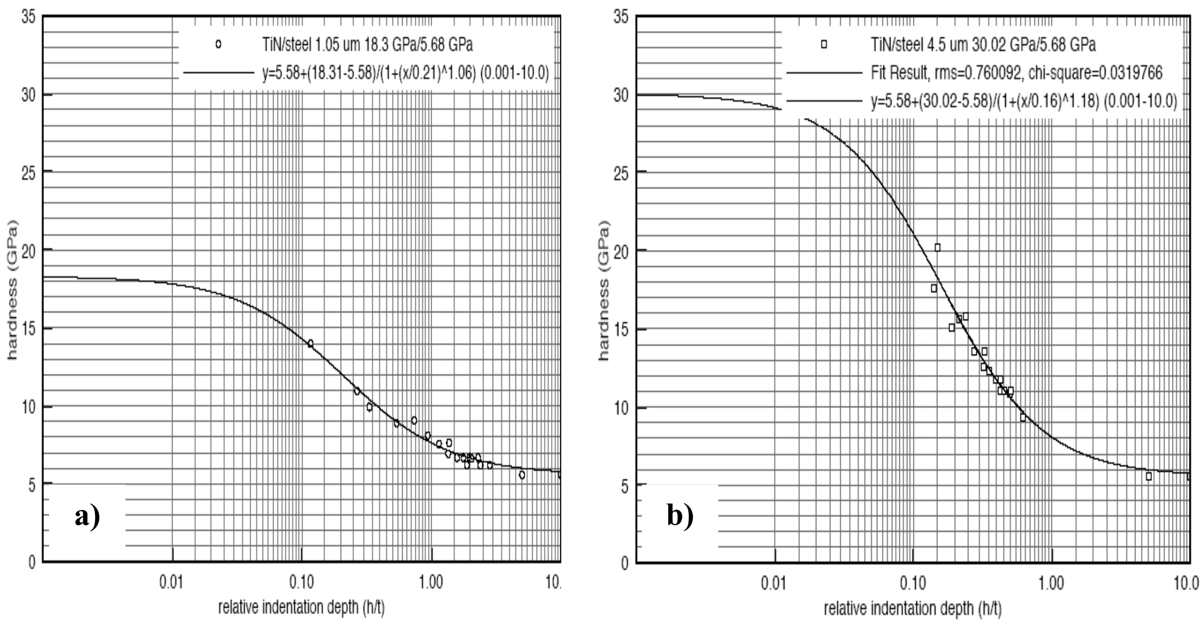

Figure 3 Composite hardness data points of a TiN coating (**a**, left) 1.05 μm and (**b**, right) 4.5 μm thick on SS420 stainless steel. The fitting parameters for the two curves are given in the legend field. Substrate hardness is 5.58 GPa in both cases. Curve (b) is much more reliable as discussed in the text.

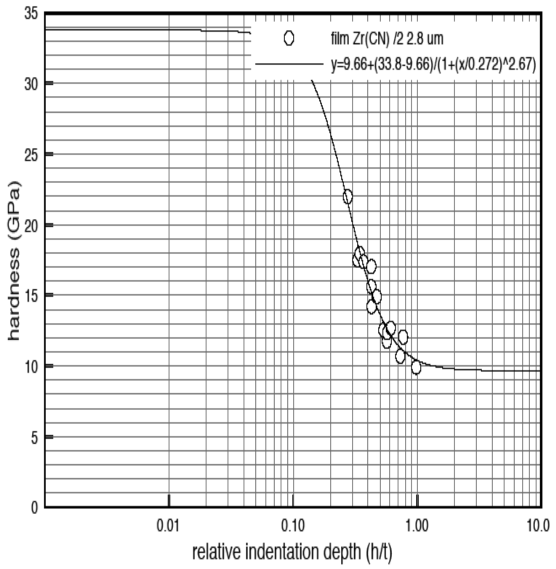

Figure 4 Composite hardness data points of a Zr(CN) coating on stainless steel. Substrate hardness unknown (9.6 GPa assumed). The fitting parameters are shown in the legend field. If a different value were chosen a fairly different curve would have been produced converging to a different bulk coating hardness on the left hand side of the plot.

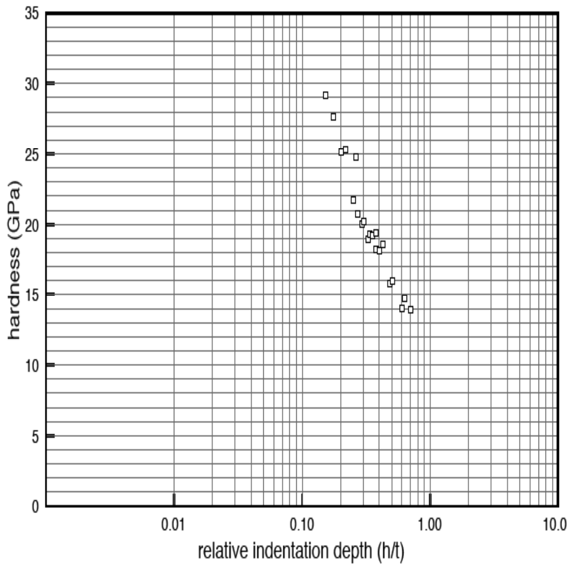

Figure 5 Composite hardness data points of a ZrN coating on stainless steel. No reasonable curve fitting can be performed due to paucity of data points in the transition regions.

5. Discussion and conclusions

The models developed in [5−6] do not include the apparent measured hardness increase due to the indentation size effect [7]. This does not reflect on the present hardness determination by solving the inverse problem since its manifestation in the microindentation range is vanishing.

First we discuss several experimental sources of error.

The nature of indentation testing demands that

(1) the films be smooth enough (mean roughness Ra<100 nm) and

(2) the substrate hardness be measured by macroindentation at high loads (> 10 N), where the contribution of a typical coating (1−5 μm) to composite hardness becomes vanishing.

Neglecting consideration (2) will fail to account for the real substrate surface and bulk hardness modified by compositional and phase changes during film deposition.

Two thickness measurement techniques have found broad application in hard coating deposition: interference microscopy, which we use, and ball-crater abrasion. Thickness data is needed to compute RID. In interference microscopy reflectance occurs over the whole specimen surface, namely the coating area, the sloped step and the bare substrate under the mask. In such observation there is no possibility to delineate the coating from any buffer sublayer. This latter could have been well seen had we used the abrasive crater ball method to cut through the coating films (and possibly using suitable decoration). The adopted thickness measurement on concomitant specimens other than those used in the hardness measurement may also introduce an additional error due to difference in growth rate if the latter is kinetically controlled by a surface reaction.

It should be borne in mind that the lower the indentation loading the smaller the deformed imprint and consequently the lower the relative accuracy of the indentation diagonal and the composite hardness value. Thus the fitting curve is intrinsically less reliable in its upper region of hardness.

In a semi-logarithmic plot the fitting curve according to the model [6] is symmetric about a center located at $(\beta_0, H_c(\beta_0))$. So in theory only the points in its lower half need be sufficient to draw such a curve. Crucial to its tracing are the transition regions where its slope changes from the maximum in the center to zero at both asymptotic ends. The lack of experimental data points in both the lower and upper transition regions makes curve fitting and plotting unsuccessful as illustrated in Figure 5. This also explains the disparity in the two curves in Figure 3 which indicate two different intrinsic film hardness values for the same TiN material. With regard to the above the curve for the thicker 4.5 μm coating should be considered more reliable. For practical applications hardness should always be measured on films thicker than 4−6 μm using microindentation thus ensuring that enough data points can fall within both transition regions [1, 5−7]. Figure 4 has its data points over a limited RID range 2.5 to 1.0. The fitted curve should be considered highly unreliable as no asymptotic behaviour can be displayed due to the lack of at least the substrate hardness.

The present work demonstrates that:

(1) Both work-of-indentation models [5, 6] can be used to solve the inverse problem of extracting intrinsic film hardness from an incomplete set of experimental data points with asymmetric distribution by non-linear curve fitting.

(2) However, curve fitting of an incomplete data set with improper distribution is very sensitive to input data. Not each set of indentation measurements can yield reasonable curve fitting and consequently provide intrisic (thickness independent) coating hardness.

(3) Coating thickness and substrate hardness must be known accurately and preferably locally.

Acknowledgement

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Improved Cathodic Arc Deposition System and Technology by Magnetic Controlled Arc Source

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Keywords: Arc deposition, vacuum arc evaporator, hard coatings, surface morphology.

Abstract. The quality and properties of PVD coatings depend strongly on the physical characteristics of the vacuum arc and induced plasma, which is determined significantly by the design of the vacuum arc deposition system. In this paper the design of a new vacuum arc evaporator is presented. It differs from the existing ones regarding geometry and construction. The evaporator is water-cooled and truncated-conically shaped. A cylindrical electrode, named auxiliary anode, is placed around it. Two electromagnetic coils, stabilizing and focusing, determine the position and movement of the cathodic spot and steer the plasma stream. With the new evaporator, the arc burns stably without any break at currents much lower than in conventional evaporators. A comparative analysis between the conventional and proposed new sources is made in respect of the working regime and quality of the obtained surface morphology. It was found that films deposited using the new evaporators contain less and smaller macroparticles, which make them preferable for vacuum arc deposition of hard coatings.

Introduction

The hard and superhard protective coatings for industrial applications are achieved by deposition of nitrides and/or carbides of different transition metals on various stainless and cutting steel in a multi-functional Physical Vapour Deposition (PVD) system.

Emphasis is placed upon the Cathodic Arc Deposition (CAD) as a PVD variant outperforming the other techniques by its higher degree of ionization, the coating density and adhesion and the overall process efficiency, a crucial issue in industrial applications. However, the presence of macroparticles in layers deposited by this method deteriorates their quality. The particle separation by combination of magnetic and electric fields has been found to be an effective method to avoid the problem. Nevertheless, this method reduces deposition rate several times and impedes the industrial application.

To improve the coating morphology by decrease of the macroparticle size and quantity and increase the process productivity, two new arc evaporators have been mounted into the CAD machine available at the Institute of Applied Physics.

This paper presents the design of the new arc evaporators in comparison to the construction and geometry of the existing ones. The principal work of both type evaporators is also discussed and compared. The advantages of the improved cathodic arc deposition system regarding the coating surface morphology are demonstrated as well.

Results and discussion

1. Physical principle of the vacuum arc deposition.

The design of the cathodic arc deposition systems is affected strongly by the particular physical properties of the vacuum arc and the plasma, which it induced.

The vacuum arc is high current electrical discharge operating at low voltages due to the high efficiency of the electron emission processes such as thermionic and field emission at the evaporator (cathode). The vacuum arc does not require any gas ambient to operate. It evaporates a material from the cathode and such way produces vapour. This vapour is ionized by the discharge forming plasma, which conducts the arc current. This current is concentrated in one or more minute spots at the cathode surface, known as cathodic spots, which number is proportional to the current value. The cathodic spots are unstable; they spontaneous extinguish and reignite at different places because of that visibly they are moving chaotically on the cathode surface. However at presence of the magnetic field ordered motion of the spots is observed primary into direction (**-IxB**) [1-3].

The cathodic spot temperature over the minute area (a few micrometers) is extremely high and significantly exceeds the boiling temperature at atmospheric pressure, which causes intensive evaporation of the cathode. Almost all of the vapour is ionized by the electrons resulted from the thermionic and field emissions. The ionization is very high and the ionized fraction is approximately 100 %.

The cathode evaporation is assisted by dispersion of liquid metal drops known as macroparticles. The presence of macroparticles worsens the quality of the deposited coatings by reason of that the decrease of their size and quantity is the main task determining the design of the arc evaporators. Because of the cathodic spots mobility, it is very important to control their position on the cathode surface during the evaporation. To avoid local preheating and to ensure the uniform wearing out of the cathode the spot movement should be controlled as well. The possible way to realize the latter is simultaneously applying the magnetic field [1-4].

2. Design and principal work description of the used vacuum arc evaporators.

In general, the arc evaporators consist of two parts: one, named vacuum part, is mounted in the vacuum chamber and a part mounted outside the chamber. The main components of the vacuum part are: a cathode, a screen and an igniter. In different construction types they differ by the shape, sizes and disposition. In present work two types of arc evaporators have been used for deposition of hard coatings: evaporator with permanent magnetic field (PMF) and evaporator with controlled magnetic field (CMF).

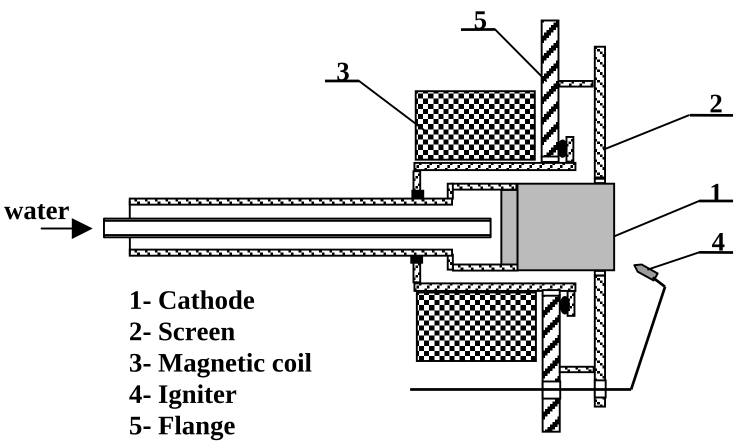

Fig. 1. Principal scheme of an evaporator with permanent magnetic field.

The principal scheme of the permanent magnetic field arc evaporator is presented in Fig. 1. This source type is usual used in common PVD systems. The cathode (1) of a PMF evaporator is cylindrical in shape and directly water-cooled. The screen (2) is placed around the cathode close to the front surface, as the interspace between them is smaller than 1 mm. The screen prevents cathodic spot movement to the cylindrical surface of the cathode. The magnetic field created by the coil (3) affect on the cathodic spot movement and it describes closed curves with irregular shape on the front surface of the cathode. Alteration of the coil current leads to changes of the most probably trajectory and the movement velocity of the spot. The igniter (4) is made from tungsten and is put in operation by an electromagnet. In the moment contact of the igniter with the cathode a current between them starts to flow. The arc is ignited in the moment of the contact break, as no high voltage is necessary. The construction of CMF evaporator significantly differs regarding the cathode-anode assembly. The CMF evaporator is schematically presented in Fig. 2. The cathode (1) has a shape of a transacted cone. As in the PMF evaporator it is directly water-cooled. The significant difference is the presence of a cylindrical electrode (2) placed around the cathode and named auxiliary anode. It is designed for the initial ignition of the arc. The other distinguishing feature is that the magnetic system consists of two coils. The stabilizing coil (4) creates magnetic field, which produces movement of the cathodic spot on the front surface of the cathode keeping it in distance from the cathode base. The focusing coil (3)

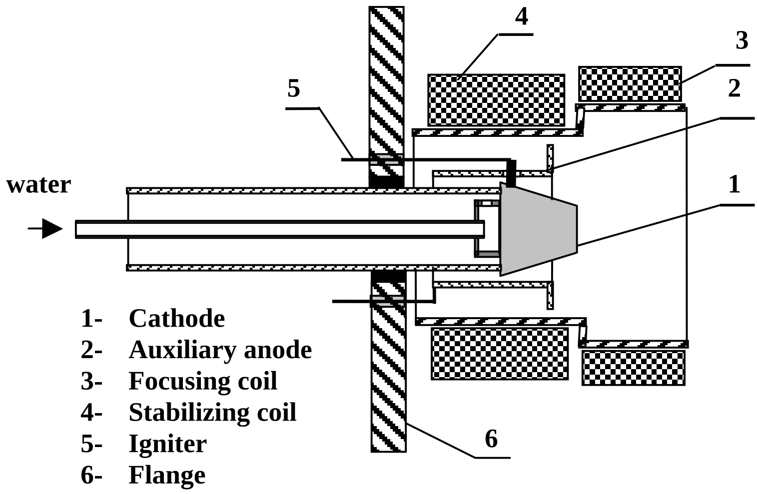

Fig. 2. Principal scheme of an evaporator with controlled magnetic field.

creates magnetic field, which lines of force are in parallel with the evaporator axis. Ions, whose velocity direction is at an angle to this axis, are affected by Lorentz forces perpendicular to the plane determined by the vectors of the velocity and magnetic field induction. Under the influence of these forces ions are moved along spiral trajectory around the evaporator axis. Besides, the focusing coil does not effect on the macroparticle movement. The latter allows decrease the macroparticles amount in the coating by increase of the distance between the cathode and the tools because the bigger part of them will be deposited on the inside surface of the evaporator and thus will not reach the tools. The igniter (5) is made from graphitized ceramic tube. The arc is ignited due to the electric breakdown after applying the high voltage impulse of 600 V to the igniter.

3. Surface morphology of coatings deposited by PMF and CMF evaporators.

In order to compare the surface morphology of coatings obtained by PMF and CMF evaporators TiN coatings have been deposited on SS 420 stainless steal substrates. Two separate experiments were performed by PMF and CMF evaporators, respectively, at the same technological regime. The samples were electro-discharge polished [5] and loaded into the vacuum chamber. After a vacuum of $5x10^{-5}$ mbar was reached the samples were heated to temperature of 300 ^{o}C. The temperature value was chosen depending on the substrate material to avoid unhardening. Immediately before the coating deposition ion cleaning of the surface was performed by applying a high voltage of 600 V to the Ti cathodes. The coating was deposited in nitrogen ambient at pressure of $2x10^{-3}$ mbar. During the deposition a bias voltage of 100 V was applied to the substrates and the temperature was maintained constant. The thickness of TiN coatings obtained by both type evaporators was measured by an interferential microscope Leitz Incident-light Microscope Interferometer and was found to be 1 μm.

The surface morphology was observed by a digital Motic MC Camera type 2000 with 2.0-megapixel resolution. The pictures are made at same magnification and are presented in Figs. 3 and 4. As it could be seen, the surface of the coating obtained by PMF evaporators (Fig. 3) is rougher with higher quantity of macroparticles. Whereas, the coatings obtained by CMF evaporators (Fig. 4) have almost smooth surface and the macroparticles quantity is smaller on the same size area. Besides, macroparticles resulted from the CMF evaporation are smaller in size and their dimensions do not differ significantly. The most widespread macroparticles have sizes lower than 90 μm, while the biggest size obtained with these coatings does not exceed 131 μm and such macroparticles are rarely on the coating surface. These dimensions are two times lower than the macroparticle size of 263 μm determined for the PMF evaporated coatings. The size (~106 μm) of the predominant macroparticles observed on the coatings deposited by PMF evaporators is bigger as well.

Summary

Comparing both evaporator types regarding the quality of the surface coating obtained as well as the exploitation characteristics, the following advantages of the magnetic field controlled source could be drown:

- The coatings morphology is improved –less quantity macroparticles with smaller dimensions are observed.

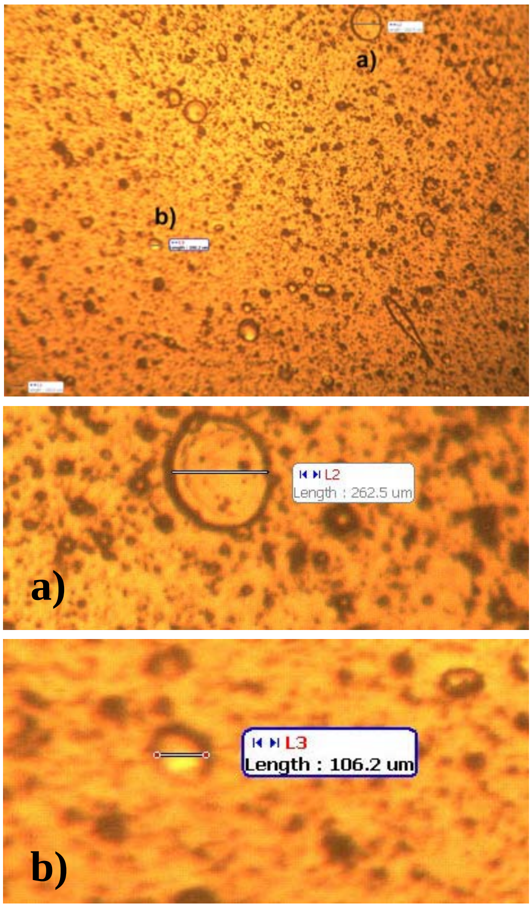

Fig. 3. Surface morphology of TiN coatings deposited by PMF evaporators; a) macroparticles with biggest sizes of 162.5 μm; b) average statistical macroparticles with sizes lower than 106.2 μm.

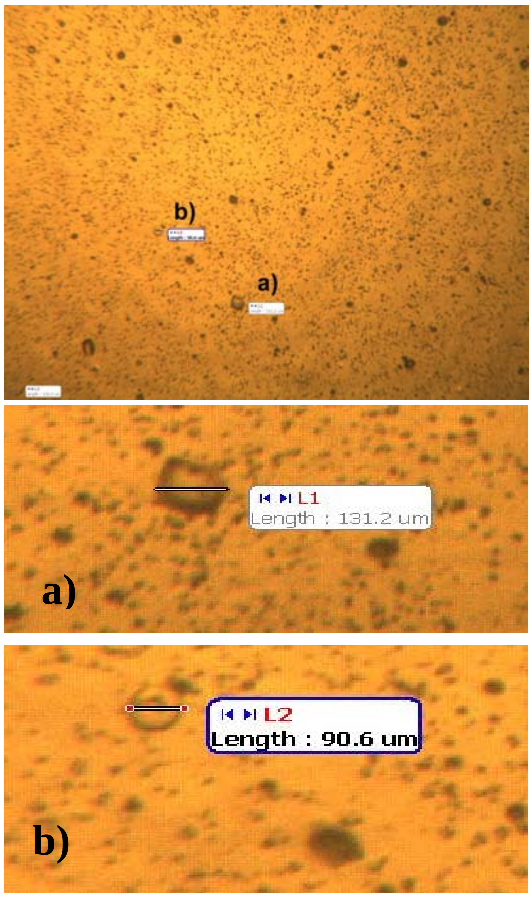

Fig. 4. Surface morphology of TiN coatings deposited by CMF evaporators; a) macroparticles with biggest sizes of 131.2 μm; b) average statistical macroparticles with sizes lower than 90.6 μm.

- The arc burns more stable without any breaks at smaller currents.
- The igniter does not stick to the cathode and process stop is avoided.
- The cathode wears out symmetrically because of that it practically does not need maintenance.

Acknowledgements

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Nanolayered Au/Ti/Al Ohmic Contacts to P-Type SiC: Electrical, Morphological and Chemical Properties Depending on the Contact Composition

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Keywords: Ohmic contacts, Al-Ti composite, Contact resistivity, AFM, XPS

Abstract. Electrical, morphological and chemical properties of nanolayered Au/Ti/Al ohmic contacts with different Ti:Al ratio are investigated. Contact resistivities of 1.42×10^{-5} $\Omega\cdot cm^2$ and 1.21×10^{-5} $\Omega\cdot cm^2$ are achieved for Au/Ti(70)/Al(30) and Au/Ti(30)/Al(70) contacts, respectively. It is found that the Ti:Al ratio does not affect the lowest resistivity value but influences on the optimal annealing temperature at which it is obtained. The different optimal annealing temperature provokes different element distributions and interface chemistry of the annealed contacts. An increase of the Al concentration in the contact composition causes essentially the surface morphology leading to an increase in surface roughness of the as-deposited and annealed contacts.

Introduction

The composition Al-Ti is commonly used as an ohmic contact to p-type 4H-SiC. The first quantitative electrical data on ohmic contacts formed using Al-Ti alloy was reported by J. Crofton et al. [1]. Although other Al-based contacts were proposed subsequently [2,3], the Al/Ti contact still remain the most applied p-type contact in SiC devices. These contacts could be obtained using an Al-Ti alloy or by subsequent deposition of Al and Ti layers. Determination of the contact composition after annealing is of interest because it could explain the origin of the ohmic behaviour. The effect of the Al-Ti alloy composition on the electrical, morphological and structural properties of ohmic contacts has been widely investigated by different research groups [1,4-6]. Nevertheless, little is known about the dependence of the contact characteristics, especially morphology and interface chemistry, on the composition of layered Al/Ti contacts [7,8].

This work presents the results from an investigation on the effect of the Ti:Al ratio in nanolayered Au/Ti/Al films upon the electrical properties, surface morphology and interface chemistry of annealed ohmic contacts. Two contact compositions, Au/Ti(70 %)/Al(30 %) and Au/Ti(30 %)/Al(70 %), have been studied and the correlation between the properties and composition ratio Ti:Al is discussed.

Experimental procedure

The contacts studied were formed on p-type 4H-SiC epitaxial layers with a thickness of 1 μm and a carrier concentration of 3×10^{19} cm^{-3}. The nanolayered metal films were successively deposited. Firstly, Al was deposited by electron beam evaporation in vacuum of $1\text{x}10^{-6}$ torr, Ti was sputtered in argon at 3×10^{-3} torr pressure and the upper Au layer in thickness of 100 nm was thermally evaporated. The Ti and Al film thicknesses were nanoscaled and chosen according to the ratios: 70 w.% : 30 w.% and 30 w.% : 70 w.% before annealing, their total thickness being 100 nm. The ohmic property formation was achieved in a furnace with resistance heating under an $Ar+1\%H_2$ gas flow. Annealing was performed at temperatures ranging from 700 °C to 1000 °C in order to obtain the lowest resistivity for each contact composition. The electrical properties were evaluated by I-V characteristics before and after annealing and by measurement of the contact resistivity using the linear transmission line model (TLM) method. Atomic force microscopic (AFM) measurements were carried out in contact mode by a NanoScope instrument. Images were usually obtained from (10×10) μm^2 scans. X-ray photoelectron spectroscopy (XPS) analysis was carried out in an ESCALAB Mk II (VG Scientific) electron spectrometer. The depth profiling was performed by Ar^+ sputtering at 3 keV and a current density of 12 $\mu A/cm^2$.

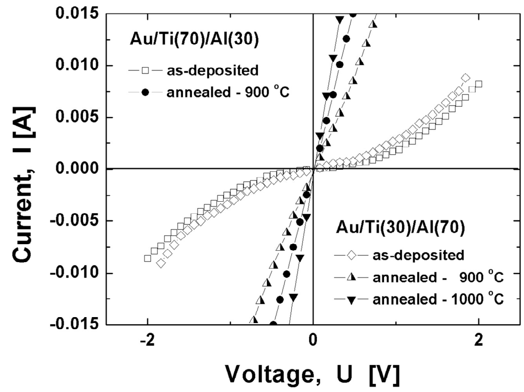

Fig. 1. I-V characteristics of Au/Ti/Al contacts with different Ti:Al ratio.

Results and discussion

I-V characteristics of both as-deposited Au/Ti/Al metallizations have a shape typical of the Schottky barrier, which determines the rectifying behaviour of the contacts despite the high epilayer doping concentration. They coincide completely, which was expectable because of the same doping concentration and the same metal film at the interface (Fig. 1). However, it was found that the composition ratio influenced on the annealing process and the dependence of the contact resistivity on the annealing temperature (Fig. 2). The effect of the annealing temperature on the ohmic behaviors was investigated as the contacts were annealed for 5 min at each temperature. Ohmic properties for the Au/Ti(70)/Al(30) contact were obtained after annealing at a temperature as low as 700 °C, while for the Au/Ti(30)/Al(70) contact they were observed at 850 °C only. The dependences of the contact resistivity on the annealing temperature differ essentially in character. The resistivity of the contact with Ti:Al=70:30 decreases smoothly with the temperature increase, reaching its lowest value of 1.42×10^{-5} $\Omega\cdot cm^2$ after annealing at 900 °C. On contrast, after annealing at the same temperature, resistivity of 5.8×10^{-4} $\Omega\cdot cm^2$ is observed for the contact with Ti:Al=30:70. The resistivity dependence on the annealing temperature is steeper for this contact and the lowest contact resistivity of 1.21×10^{-5} $\Omega\cdot cm^2$ is obtained after annealing at 1000 °C. This value does not differ essentially from the one achieved for the contact with a lower Al amount. The result is confirmed by the I-V characteristics measured on the contacts with the lowest resistivity, which have the same slope and coincide almost completely (Fig. 1). The I-V characteristic of the Au/Ti(30)/Al(70) contact annealed at 900 °C is presented for comparison in Fig. 1. The smaller slope corresponds to the higher contact resistivity. The result shows that the different Ti:Al composition ratio of nanolayered Au/Ti/Al contacts does not affect the lowest resistivity value but initiates on the annealing process and the temperature at which this resistivity is achieved. The higher Al amount into the contact determines the higher optimal annealing temperature. We suppose that these dependencies relate to the Al diffusion during annealing which may limit the reactions at the SiC interface.

AFM measurements revealed a strong dependence of the surface morphology on the Ti:Al ratio. It was found that the higher Al amount in the as-deposited contact caused rising of the surface roughness by more than 2.5 times. RMS surface roughness of 8.3 nm and 22.3 nm was determined for as-deposited Au/Ti(70)/Al(30) and Au/Ti(30)/Al(70) contacts, respectively (Figs. 3a and 4a). We suppose that this distinction is because of the specific feature of Al to form drops during evaporation. A thicker Al film

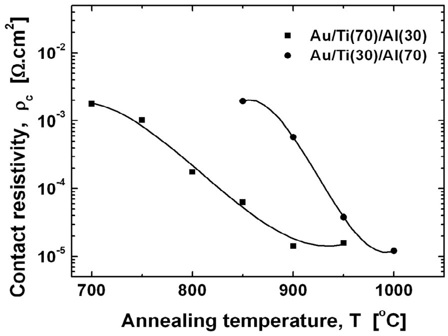

Fig. 2. Dependence of the resistivity of Au/Ti/Al contacts with different Ti:Al ratio on the annealing conditions.

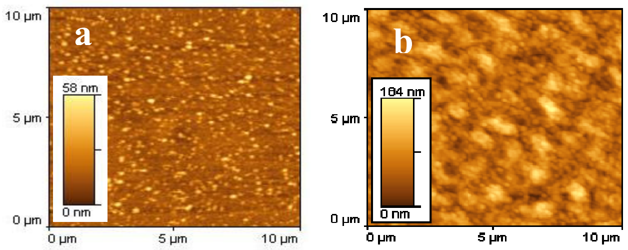

Fig. 3. AFM images of as-deposited (a) and annealed at 900 °C (b) Au/Ti(70)/Al(30) contacts.

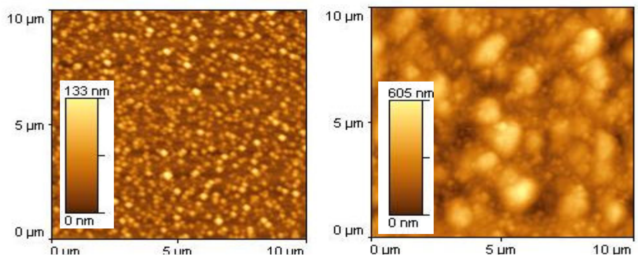

Fig. 4. AFM images of (a) as-deposited and (b) annealed at 1000 °C Au/Ti(30)/Al(70) contacts.

presupposes a higher drops' number, which affects the surface morphology. After annealing the surface roughness increases with the annealing temperature and the Al amount in the contact. Annealed at 900 °C Au/Ti(70)/Al(30) contact had a surface roughness of 27.7 nm and a main grain size around 800 nm (Fig. 3b), while RMS of 80.3 nm and a grain size around 1.2 µm were measured for the Au/Ti(30)/Al(70) contact after annealing at the same temperature. Further increase of the annealing temperature up to 1000 °C caused an increase in surface roughness and grain size to 101.2 nm and 1.6 µm, respectively (Fig. 4b).

XPS depth analysis was performed to investigate the contact composition and interface chemistry of Au/Ti(70)/Al(30) contact annealed at 900 °C and Au/Ti(30)/Al(70) contact annealed at 1000 °C. These contacts showed the lowest resistivity (Fig. 5). As can be seen, the different Ti:Al ratio and resulting different annealing temperatures led to remarkable differences in element distribution and interface chemistry of both ohmic contacts. (The different sputtering time is due to the different sputtering ratio, not different contact thickness.) The XPS depth profiles allow dividing the contact structure into three regions: surface, film and interface. In both contacts strong Al diffusion to the surface promoted by the thermal treatment was obtained. At the very surface existence of Al_2O_3 was detected in both contacts. Besides, in the Au/Ti(30)/Al(70) contact additional presence of SiO_x was obtained. With prolonged sputtering the Ti:Al=70:30 film (Fig. 5a) showed a simultaneous increase in gold and titanium concentrations. The shift of the binding energy of gold in this region up to 84.7 eV was probably connected with the change in chemical surroundings of the Au atoms by Ti atoms and we associated it with formation of an Au(35 at%)+Ti(42 at%) alloy. The positions of C1s and O1s peaks revealed presence of TiC and TiO in the film region. Quite a different element distribution was observed for the Ti:Al=30:70 contact (Fig. 5b). The film region consisted mainly of Au and Al as a decrease in Al and increase in Au concentrations was detected. The concentrations of Ti, Si and C remained almost constant and formation of Ti_3SiC_2 [7] was possible. Simultaneously a shift of the Au4f peak core level to a higher binding energy (84.2 eV) was detected up to 1200 min sputtering. This could be associated with change in chemical surroundings of the Au atoms by Al. The formation of an Au-Al alloy is not excluded. Between 1200 and 1800 min sputtering, Au in metal state and formation of TiC has been detected. The interface region of the Ti:Al=70:30 contact

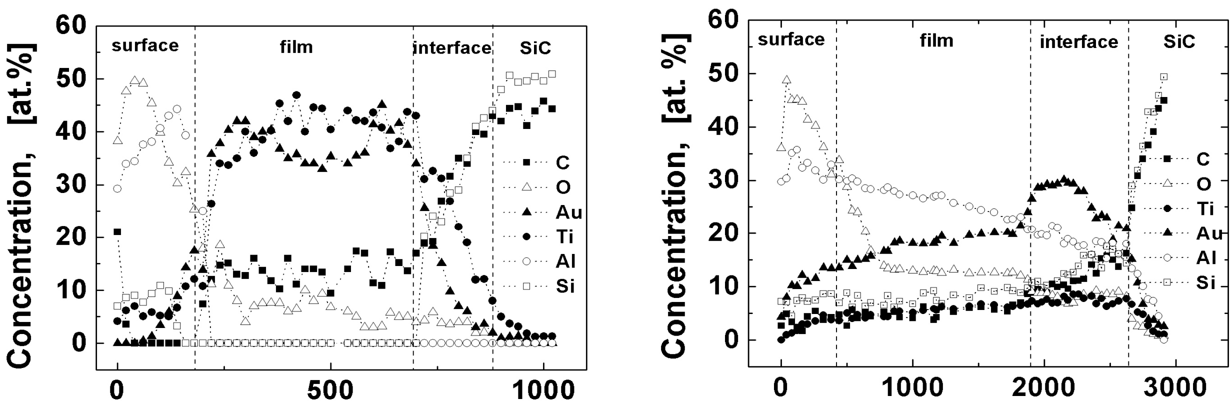

Fig. 5. XPS depth profiles of Au/Ti/Al contacts with different Ti:Al ratio: on the left -Au/Ti(70)/Al(30) and on the right - Au/Ti(30)/Al(70).

has been found to be narrow. The annealing at 900 ^{o}C causes dissociation of the SiC surface and dissociated carbon interacts with Ti forming TiC. The interface region for the contact with a Ti:Al=30:70 ratio annealed at 1000^{o}C is remarkably wider. Along the interface increase of Au, Si and C concentrations have been observed, accompanied by a decrease in Al concentrations. The shift of the Au4f binding energy to the higher values has been determined, which could be connected with silicide formation. Appearance of TiC as a result of the SiC surface dissociation has been also detected. No carbon in graphite state and nonbonded silicon has been obtained.

Summary

The results from the investigation on the electrical properties of nanolayered Au/Ti(70)/Al(30) and Au/Ti(30)/Al(70) ohmic contacts revealed that the different Ti:Al ratios did not affect the lowest resistivity value achieved. We associate the arising ohmic behaviour with the decrease of the barrier height as a result of TiC formation at the metal/SiC interface during annealing. Presence of TiC at the interface with SiC has been found by XPS analysis in both contacts. However, the rise of the Al amount in the initial contact film causes an increase in the optimal annealing temperature at which the lowest resistivity is obtained. As a result of the higher annealing temperature (1000 ^{o}C) of the contact with Ti:Al=30:70 a slight diffusion of Al into the SiC surface was observed by contrast with Ti:Al=70:30 contact. It could be supposed, in analogy with the Ti-Al alloyed contacts annealed at the same temperature [6] that in the annealed Ti/Al layered contacts Al is also distributed like spikes near the SiC surface. The kind of this distribution can be analysed by other techniques that have not been used in this study. AFM study revealed that the increase of Al concentration in the contact composition influenced essentially the surface morphology leading to an increase in surface roughness and lateral dimensions of the contact features. This could be very critical in the nanolayered metal films and contacts with very small areas, which are used in nanosized devices.

Acknowledgements

The support from the European project INCO – CT- 016805 is gratefully acknowledged. The authors express their gratitude to Dr. Petia Weih from the Technical University of Ilmenau for the AFM measurements.

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Project no.: INCO-CT-2005-016805

Project acronym: RTCNANOHARD

Project title: **Strengthening the Research and Technological Capacity in the Field of Nanostructured Thin Films, Hard and Superhard Coatings**

Instrument: Specific Support Action - 2

Thematic Priority: 3

Final management report

Period covered: from April 2005 to September 2007

Date of preparation: 05.11.2007

Start date of project: 01.04.2005

Duration: 30 months

Project coordinator name: Roumen Kakanakov
Project coordinator organization name:
Institute of Applied Physics,
Bulgarian Academy of Sciences

3. Final management report

Section 1- Justification of the major cost items and resources deployed for the project fulfilment during the project

3.1. Description of the work during the project

Management work for executing WP1: Project management activities

With the starting of the project was created management team consisting of project coordinator and work package leaders:

WP1 – Dr. Roumen Kakanakov-Project coordinator
WP2 – Dr. Peter Sveshtarov
WP3 – Dr. Liliana Kolaklieva
WP4 – Dr. Roumen Kakanakov
WP5 – Dr. Gencho Sarov

During the second year Dr. Gencho Sarov was changed from Dr. Tetyana Cholakova.
During the execution of the project a lot of researchers, engineers and technologists were working. Also early stage scientists were participating in the project as follow: M.Sc. Maria Enevska, the Ph.D. students Nina Hristeva, Hristo Kisiov, Nikolay Petkov and Vassiliy Chitanov.
During the project 48 person-months on total value of 11961 Euro was paid from the project founds. The rest person-months were paid from founds of the Institute of Apply Physics.
Due to this was created functional Physical Vapour Deposition (PVD) equipment corresponding to the European standards. For this PVD was developed technology for deposition of nanostructured thin films, hard and super hard coatings from nitrides and carbides on instruments and details from metals, semiconductors and isolators.

Management work for executing WP2: Exchange of personnel: researchers, Ph.D. students and postdoctoral researchers to carry out specific research experiments

The fulfilment of the project opened horizons for exchange of leading experts, researchers and specialists. A lot of specialists came and visited IAP under work meetings and workshops. This gave opportunity for discussions and exchange of state of the art ideas, experience and themes contributing to speeding up and embedding the equipment and technology. All this further for open discussions and receiving of knowledge's locally at the Institute without sending our specialists on business trips and save us "Travel" costs, which were redirected to "Equipment".
The main topics of the three meetings held during the second year were hardness and adhesion, characterization of layers by TEM, SEM and AFM. The second meeting was client oriented with representatives of the firms FESTO and AREXIM, which are our clients of hard and superhard coating services on tools.
An important Business trips to Belgrade, New Castle, Thessaloniki, Minsk, Moscow and Sankt Petersburg were made. On June 2007 Dr. Roumen Kakanakov was at the Ioffe Physical-Technical Institute, Sankt Petersburg Russia on meeting with Academician J.I.Alferov, a Nobel Prize Laureate for Physics for 2000, where questions concerning the growth and characterization of nanosized heterostructures of GaN/GaAIN were discussed.
It was made also exchange of Ph.D. students. For example two Ph.D. students from the Institute of Micro and Nanotechnologies, Technical University Ilmenau visited IAP. The aim of the visit

of Florentina Will and Katja Tonicsh was introducing and training in technology for deposition of nanolayerd thin metal films for sub-micron devices. The both Ph.D. students shared their experience for characterization of thin films. This visit was only one of the planed exchanges of scientists between both Institutes.

<u>Management work for executing WP3: Organization of workshops and conferences in order to exploit and disseminate of research results</u>

During the execution of the project were organised three scientific events (two workshops and one conference) on International level. In these scientific events were participated leading scientists from Germany, United Kingdom, Russia, Belgium, Belarus, Portugal, Sweden, Switzerland, Greece, Turkey, Republic of Macedonia and Bulgaria. The presentations were edited and published in Proceedings.
The workshop NANOHARD 2005 "New trends in development of nanostructered thin films, hard and super hard coatings" was held from 19.10.2005 to 21.10.2007 in the Complex Philippopolis, Plovdiv and was attended by 36 international participants. Among them were Prof. Dr. Dr.h.c. Stan Veprek (Technical University of Munich, Germany), Prof. Luis Rebouta (Universidade do Minho, Portugal) and Prof. Erik Janzen (Linkoping University, Sweden). Bulgarian scientists from different Institutes of the Bulgarian Academy of Science, Sofia University and IAP took part at the workshop. The success of the NANOHARD 2005 was due to the high scientific level of the lectures and the followed discussions ensured by the session chairpersons.
The Conference NANOHARD 2006 was with topic "New trends in development of nanostructered thin films, hard and superhard coatings". It was held from 28.05.2006 to 31.05.2006 in Sozopol, Bulgaria. Around 37 scientists, engineers and specialists from 6 countries attended this Conference. Invited lectures were again Prof. Dr. Dr. h.c. Stan Veprek, Prof. Luis Rebouta and Prof. Dr. E.K. Polychroniadis (Aristotel University of Thessaloniki, Greece) and Assoc. Prof. Dr. Cevat Sarioglu (Marmara University, Turkey). Except the Bulgarian scientists, in this conference took part and representatives of two companies operating in the field of hard coatings Milko Angelov Consulting, Bulgaria and Titanit, Turkey.
The Workshop NANOHARD 2007 "Development, characterization and industrial application of nanostructured thin films, hard and superhard coatings" was from 13.05.2007 to 16.05.2007 in Velingrad, Bulgaria. The workshop was attended by 33 scientists from 7 Research Institutes and 7 Universities from 8 countries. Prof. Steve Bull (Newcastle University, UK), Prof. Dr. Dr.h.c. Stan Veprek and Dr. Volker Cimalla (Technical University Ilmenau, Germany) were invited talkers. One of the main topic discussions in NANOHARD 2007 was the industrial application of nanostructured thin films, hard and superhard coatings. This discussion was attended by specialists from 5 industrial companies working in this field: CSM Instruments SA (Switzerland), Plasma Ltd. (Republic of Macedonia), FESTO (Bulgaria), AREXIM (Bulgaria) and Milko Angelov Consult.
Generally for organization and leading of NANOHARD 2005, 2006 and 2007 was spent 20158.82 Euro at planed 22000 Euro.

<u>Management work for executing WP4: upgrade, renewal and design of the existing S&T equipment</u>

The main task of the project was creation of specialised Physical Vapour Deposition (PVD) equipment for deposition of nanostructured thin films hard and superhard coatings by electric arc deposition (EAD). In some specialised papers is used the terminology cathodic arc deposition (CAD). For this purpose was used basic high vacuum system available at Institute of Applied

Physics (IAP). It was equipped with 500 litres two-wall water cooled vacuum chamber, including capacity substrate planetary holder, two resistant heaters (2x3 kW) and all necessary power supplies. On the periphery of the Vacuum chamber were situated symmetrically two couples arc cathodes, in which were embed targets of Ti, Al, Cr, Zr and their alloys. The first couple cathodes were standard equipped with one stabilising electromagnetic coil. The second couple arc cathodes were original decision of the team equipped with two electromagnetic coils, stabilising and focusing and target with special profile. By using three mass flow controllers (range 0-500 sccm) in the vacuum chamber can be inputted exactly dozed clean gasses: Ar, N and methane. Before deposition of the coatings the instruments and details can be preliminarily cleaned and heated with plasma and ion bombardment (voltage up to 1200 V). Due to the Siemens controllers and the appropriate software the process of deposition of coatings was fully automated. In this way coatings of nitrides, carbides and carbonitrides were obtained with stable parameters. The grown coatings had thickness of 0.5-5 μm and microhardness of 20-45 GPa.
For obtaining coatings of good quality the preliminary processing of the samples is important. For this purpose equipment and technology for electrodischarge polishing was developed. This equipment is unique for Bulgaria. Using ecologically clean solutions with properly chosen catalyst and electrical conditions much better polishing of the samples was achieved, which included cleaning and smoothing of the surfaces. Three units were produced for electrodischarge polishing: a prototype (7 kW), a semi-industrial (20 kW) and industrial unit (30 kW). The created equipment for polishing is used not only for preparing of the samples for electric arc deposition, but for fulfilment of polishing orders of companies.
Additionally a specialised system for magnetron sputtering for growing nanostructered thin films for special purposes was put in operation. Regarding this in the third year of the project an automatic input flow valve and a second magnetron was mounted in the vacuum machine for magnetron sputtering available at IAP, which helped for deposition of specialised nanostructured thin films.
Two diamond indenters were bought to be used in microhardness measurements for quality assessment and certification of the deposited thin films and hard and superhard coatings.
As a final result after the project implementation we have working PVD equipment that has the same class of quality as leading European companies. We have unique equipment for EDP, which is not offered by any other company on the European market. For the development of these equipment units 79702.65 Euro direct costs and 23283.28 Euro indirect costs from the project were used. This imposed resources from personal and travel items to be redirected to equipment costs. If it is accepted, that the basic high vacuum system available at the IAP is valued at 100000 Euro, then the total value of the PVD equipment comes to about 200000 Euro. At the same time we have to note, that the cheapest PVD equipment on the European market costs about 600000 Euro.
By the end of the project we have a completely developed functioning innovative centre, where technological services and training are performed on the request of different firms.

Management work for executing WP5: implementing a monitoring and evaluation system.

During the project realization a set of indicators was defined which reveal the progress of the project implementation and methods for measuring of these indicators were chosen: physical indicators to measure hard and superhard coatings (*thickness, adhesion and hardness*); performance indicators to measure the results obtained in terms of objectives (*increased wear resistance of cutting tools, improved scientific and educational potential of IAP, renovated multi-functional PVD system suitable for high quality coatings and adaptability level of the upgraded system to industrial application*); financial indicators to measure the amount of investments to improve the innovation system (f*ixed cost indicator and variable cost indicator*).

1. Physical indicators measure: Various binary and ternary materials obtained by Cathodic Arc Deposition: nitrides, carbides, carbonitrides and bi-phase composites based on these were investigated and evaluated. They were deposited on different types of substrates. A systematic study of the influence of the main deposition parameters (reactive gas pressure, substrate bias, arc current) on the film properties was undertaken in order to optimize the cathodic arc deposition process.

2. Performance indicators measure: A young bachelor of electronics has begun a Master study and entered its completion phase at the Technical University of Plovdiv. A young physicist with a Master degree was trained to operate and maintain the renovated automatic deposition plant. Two senior scientists of IAP's staff were also trained into the same plus the measurement and characterization of hard thin films. An experienced electronic engineer was employed and assigned the task of maintaining, repairing and supervising the automated PVD equipment. During the project duration five doctorants were trained and educated in the field of thin film physics and process automation. An Associate Professor from the Technical University of Plovdiv worked on problems related to the control and automation of technological processes and was officially appointed to work at the Institute of Applied Physics. Four IAP specialists visited leading European laboratories. Two of our scientists participated in the 6^{th} European Conference on Silicon Carbide and Related Materials ECSCRM 2006, Newcastle, UK.

Multifunctional PVD system renovation: Four arc sources (two of them of a new generation) were constructed, mounted in the vacuum chamber and run. A magnetron deposition system was constructed to deposit nanostructured coatings. The most important step was the purchase of the needed hardware and software for implementing the full automation of the technological process.

The multifunctional PVD system was renovated and used for the production of nanostructured hard and superhard coatings.

The adaptability of the upgraded PVD system to industrial application was evaluated by (1) the achieved capability to deposit the chemical compounds for hard coatings, (2) the reproducibility of the coating deposited upon parts in a single batch and from batch to batch and (3) the ability to run coating services according to a customer's specification. At the end of the project our renovated multifunctional PVD system provides the base for technological transfer to industry.

3. Financial indicators measure: The direct cost of 79702.65 Euro was invested for upgrading the existing system to a multi-functional PVD system during the whole reporting period. The indirect cost of 23283.28 Euro was invested for cathode arc coating materials (Ti, Ti-Al, Cr, Zr, etc.), chemicals, gases, pump oil, electric power and etc.

4. Quality assurance of the project: By the end of the project implementation all deliverables were completed successfully and no deliverable was rejected.

3.2. Explanatory note on major cost items.

During the project (01.04.2005-30.09.2007) PVD equipment and technology for electric arc deposition of nanostructered thin films, hard and superhard coatings were created. For the building this PVD equipment a basic high vacuum system priced about 100000 Euro belonging to the Institute of Applied Physics (IAP) was used. From the founds of the project equipment, building elements and modules amounting to **69781.25 Euro** were bought, which were used for upgrading and transformation of the basic high vacuum system to PVD equipment. The important items from the bought equipment, building elements and modules are given in the next table.

Bulding elements and moduls for Electric arc deposition equipment		
№	Name of the article	Cost in Euro without a VAT
1	Mechanical Vacuum pump	9,460.00
2	Acceleration pump	10,797.00
3	Vacuum meters, Pirani (2 pcs) and Penning (1 pcs)	2,327.00
4	Producing of planetary mechanism	2,551.35
5	Measurement Head	291.97
6	Designing and producing heater elements for vacuum system	3,266.64
7	Hastings Flowcontroller HFC-302	1,915.00
8	Electric arc sources (cathodes 2 pcs).	12,271.00
9	Modul for cathodes control	2,060.00
10	Supply of cathodes	2,096.00
11	Upgrade of power supply for electric arc source	1,022.58
12	Modul work voltage “BIAS”	2,541.12
13	Controller for management of the electric arc deposition process	2,530.89
14	Block control of the arc ignition	1,328.12
15	Designing, mounting and testing of passing flanges for electric arc cathodes	102.26
16	Computer system with software for PVD system	1,049.87
17	Designing and producing of double channel former arc starter	623.78
18	Upgrade and Control of PVD equipment	6,670.61
19	Indentor for microhardnes equipment	796.25
20	Building elements, modules, machine parts and electrone components	6,079.81
	Total	**69,781.25**

For creating of nanostructered thin films for special purposes, additionally a specialised system for magnetron sputtering was put in operation. For this purpose was used basic high vacuum system with turbomolecular pump of value about 70000 Euro belonging to the IAP. From the founds of the project equipment, building elements and modules of value **2075.30 Euro** was bought, which was used for transformation of the basic high vacuum system to magnetron sputtering equipment. The bought building elements and modules are given in the next table.

Bulding elements and moduls for magnetron spattering equipment		
№	**Name of the article**	**Cost in Euro without a VAT**
1	Producing and mounting of vacuum fixture	230.08
2	Precise automatic valve ALV 01, set.	766.94
3	Digital Controller with supply	578.28
4	Building elements and machine parts	500.00
	Total	**2,075.30**

For obtaining coatings of good quality is of great importance the advance preparation of the examples. For this purpose was developed equipment and technology for electrodischarge polishing. This equipment is unique for Bulgaria. Using ecologically clean solutions with properly chosen catalysts and electrical conditions much better polishing of the samples was achieved, which include cleaning and smoothing the surface. Three units were produced for electrodischarge polishing: prototype (7 KW), semi-industrial (20 KW) and for industrial application (30 KW). The created equipment for polishing was used not only for preparing the samples for electric arc deposition, but also for fulfilling polishing orders from private companies. From the founds of the project building elements, modules and machine parts of value **7846.10 Euro** were bought, which were used for building this unique equipment. The bought building elements, modules and machine parts are given in the next table.

Building elements and moduls for electrodischarged polishing equipment		
№	**Name of the article**	**Cost in Euro without a VAT**
1	Three-phase transformer TGR 20 kVA	1,022.58
2	Transformer, 30 kVA	1,906.10
3	Supply of discharge polishing	511.29
4	Producing a tank for electrodischarge polishing (EDP)	265.87
5	Control of equipment for EDP	664.68
6	3TC481700BP0 Circuit - breaker	255.64
7	Repair of electric system	1,533.88
8	Electric tools and modules	686.06
9	Building elements and machine parts	1,000.00
	Total	**7,846.10**

The total value of the spent resources from the project founds for creating the equipment was **79702.65 Euro**.

For putting the three units in operation and creating of the technologies of cathodic arc deposition, special magnetron sputtering and electrodischarge polishing materials and consumables needed to be purchased of totals value **23283.28 Euro**. The higher costs were for buying targets of Ti, Al, Cr, Zr and their alloys of purity 4N, Ar, N, H_2 and methane gases of 6N purity, vacuum oil, vacuum fixture and etc.

As a final result after fulfilment of the project we have working equipment that has the same class of quality as leading European one. On this equipment technology, which can be used for industrial application was developed.

During the execution of the project three scientific events of International level were organized (two workshops and one conference) NANOHARD 2005, 2006 and 2007. **20158.82 Euro** were spent on these**.** For business trips of our specialists in leading European laboratories were spent **9886.94** Euro. The total costs for Travel were **30045.76 Euro.** The unused 26584.24 Euro from this item were redirected to Equipment.

The total sum of personal costs during the project was **11961.00 Euro**. The unused amount of 4464.00 Euro from this item was also redirected to equipment.

The total amount of costs for management was **8173.96 Euro** and **1970.15 Euro** for other costs.

The total value of the costs, which were accounted for the execution of the project was **155136.80 Euro.**

The main result from the fulfilment of the project is the creating of working equipment and new technologies, which were united in Innovation centre at the Institute of Applied Physics for research, development, industrial applications, education and knowledge dissemination. In this Innovation centre technological orders for deposition of hard and superhard coatings were carried out for firms. It will handle the transfer of technologies. Thanks to the created good professional contacts with leading European specialists and organizations successful cooperation of bilateral and versatile character can be realised between the Innovation centre and other scientific and industrial organizations in the European community.

Section 2 – Form C Financial statement per activity for the contractual reporting period

Form C - Model of Financial Statement per Activity (to be filled by each contractor)			
Type of instrument	Specific Support Action	**Type of Action (if necessary)**	
Project Title (or Acronym)	Strengthening the Research and Technological Capacity in the Field of Nanostructured Thin Films, Hard and Superhard Coatings	**Contract n°**	16805
Contractor's Legal Name	Institute of Applied Physics		
Legal Type			
Contact Person	Roumen Kakanakov	**Telephone**	
Telecopy		**E-mail**	ipfban@mbox.digsys.bg
Cost model used (AC//FC or FCF)	FC	**Indirect costs(Real or Flat Rate of 20% of Direct costs, except subcontracting)**	Real indirect cost
Period from	01.04.2005	**To**	30.09.2007

1- Resources (Third party(ies))			
Are there any resources made available on the basis of a prior agreement with third parties identified in Annex I of the contract? (Yes / No)			No
If Yes, please provide the following information			
Third Party 1 (Y1) Legal Name		**Cost model used**	
Third Party 2 (Y2) Legal Name		**Cost model used**	
Third Party 3 (Y3) Legal Name		**Cost model used**	
Third Party 4 (Y4) Legal Name		**Cost model used**	

2- Declaration of eligible costs (in ¬)
Please complete only the activity covered by the relevant instrument (and type of action) indicated above and as mentioned in Article II.25 and/or in Annexes I and III of the contract.
If you are a contractor using the additional cost model (AC):
- indicate only your additional eligible costs, except for Management of the Consortium Activity for which you may indicate your full eligible costs;
- do not declare eligible direct additional costs specifically covered by contributions from third parties as mentioned in Articles II.20 and II.23.a and b of the contract.
If you are a contractor using a full cost model (FC/FCF), indicate your full eligible costs.
The costs declared should distinguish between direct and indirect costs.
If necessary, adjustments to previous period(s) may be included where appropriate.

Type of Activity

	Research and Technological Development / Innovation (A)		Demonstration (B)		Training (C)		Management of the Consortium (D)		Other Specific Activities (E)		Total (F) = (A)+(B)+(C)+(D)+(E)	
	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)
Direct costs							8173,96		115884,17		124058,13	0,00
Of which subcontracting											0,00	0,00
Indirect costs									31078,67		31078,67	0,00
Adjustments to previous period(s)											0,00	0,00
Total costs	0,00	0,00	0,00	0,00	0,00	0,00	8173,96	0,00	146962,84	0,00	155136,80	0,00

3- Declaration of receipts (in €)
If you are a contractor using the additional cost model (AC), indicate only receipts covered by Article II.23.c of the contract.
If you are a contractor using a full cost model (FC/FCF), indicate receipts covered by Article II.23 of the contract.
If a receipt is not allocated to an activity

	Type of Activity											
	Research and Technological Development / Innovation (A)		Demonstration (B)		Training (C)		Management of the Consortium (D)		Other Specific Activities (E)		Total (F) = (A)+(B)+(C)+(D)+(E)	
	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)	Contractor	Third Party(ies)
Total receipts											0,00	0,00

4- Declaration of interest generated by the pre-financing (in €) **To be completed only by the coordinator.**	
Did the pre-financing (advance) you received by the Commission for this period earn interests? (Yes / No)	No
If yes, please mention the amount (in €)	

5- Request of FP6 Financial contribution (in €)	
For this period, the FP6 Community financial contribution requested is equal to (amount in €)	147234,96

6- Audit certificates				
According to the contract, does this Financial Statement need an audit certificate (or several in case of Third party(ies)) delivered by independent auditor(s)? (Yes / No)				Yes
If Yes, does this(those) audit certificate(s) cover only this Financial Statement per Activity? (Yes / No)				No
If No, what is the periodicity covered by this(those) audit certificate(s)?		**From – To**	01.04.2007	30.09.2007
What is the total cost of this(those) audit certificate(s) (in €) per independent auditor(s) ?				
Audit certificate of the contractor (X)				
Legal name of the audit firm	Lyubka Shumanska reg No 0077	**Cost of the certificate**	400,00	
Audit certificate(s) of the third party(ies) (Ys) (if necessary)				
Y1: Legal name of the audit firm		**Cost of the certificate**		
Y2: Legal name of the audit firm		**Cost of the certificate**		
Y3: Legal name of the audit firm		**Cost of the certificate**		
Y4: Legal name of the audit firm		**Cost of the certificate**		
		Total (Z) = (X) + (Ys)	400,00	

Reminders:
The cost of an audit certificate is included in the costs declared under the activity "Management of the Consortium".
The required audit certificate(s) is(are) attached to this Financial Statement.

7-Conversion rates

Costs incurred in currencies other than EURO shall be reported in EURO.

Please mention the conversion rate used (only one choice is possible) – Please note that the same principle applies for receipts.

Contractor	
- Conversion rate of the Date of incurred actual costs?	Yes
- Conversion rate of the first day of the first month following the period covered by this Financial Statement?	No
Third Party(ies) (if necessary)	
Third Party 1 (Y1)	
- Conversion rate of the Date of incurred actual costs?	Yes
- Conversion rate of the first day of the first month following the period covered by this Financial Statement?	No
Third Party 2 (Y2)	
- Conversion rate of the Date of incurred actual costs?	Yes
- Conversion rate of the first day of the first month following the period covered by this Financial Statement?	No

Third Party 3 (Y3)	
- Conversion rate of the Date of incurred actual costs?	Yes
- Conversion rate of the first day of the first month following the period covered by this Financial Statement?	No
Third Party 4 (Y4)	
- Conversion rate of the Date of incurred actual costs?	Yes
- Conversion rate of the first day of the first month following the period covered by this Financial Statement?	No

8- Contractor's Certificate

We certify that:

- the costs declared above are directly related to the resources used to reach the objectives of the project ;
- the receipts declared above are directly related to the resources used to reach the objectives of the project ;
- the costs declared above fall within the definition of eligible costs specified in Articles II.19, II.20, II.21, II.22 and II.25 of the contract, and, if relevant, in Annex III and Article 9 (special clauses) of the contract ;
- the receipts declared above fall within the definition of receipts specified in Article II.23 of the contract ;
- the interest generated by the pre-financing declared above falls within the definition of Article II.27 of the contract ;
- the necessary adjustments, especially to costs reported in previous Financial Statement(s) per Activity, have been incorporated in the above Statement ;
- the above information declared is complete and true ;
- there is full supporting documentation to justify the information hereby declared. It will be made available at the request of the Commission and in

Contractor's Stamp	Name of the Person responsible of the work	Name of the duly authorised Financial Officer
Институт по приложна физика ПЛОВДИВ	Roumen Kakanakov	Radka Todorova
	Date	**Date**
	05.11.2007	05.11.2007
	Signature	**Signature**

Section 3 – Summary Financial Report

Summary Financial Report																			
Type of Instrument	SSA	Project Title (or Acronym)	Strengthening the Research and Technological Capacity in the Field of Nanostructured Thin Films, Hard and Superhard Coatings												Contract Nº	16805			
Reporting period number		3	From (dd/mm/yyyy)	01.04.2005						To (dd/mm/yyyy)		30.09.2007						Page	1/1
				Type of activities															
Contractor nº	Organisation Short Name	Cost model used	Eligible costs (in €)	Research and Technological Development / Innovation (A)		Demonstration (B)		Training (C)		Management of the consortium (D)		Other Specific Activities (E)		Total eligible costs (F)=(A)+(B)+(C)+(D)+(E)		Receipts		EC contribution	
				Contractor	Third party(ies)	Contractor	Third party(ies)	Contractor	Third party(ies)	Contractor	Third party(ies)	Contractor	Third party(ies)	Contractor	Third party(ies)	Contractor	Third party(ies)	Maximum	Requested
			Direct eligible costs	0,00	0,00	0,00	0,00	0,00	0,00	8 173,96	0,00	115 884,17	0,00	124 058,13	0,00				
			of which direct eligible costs of subcontracting	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*				
1	Institute of Applied Physics	FC	Indirect eligible costs	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	31 078,67	0,00	31 078,67	0,00	0,00	0,00	147 234,96	147 234,96
			Adjustment on previous period(s)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
			Total eligible costs	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*0,00*	*8 173,96*	*0,00*	*146 962,84*	*0,00*	155 136,80	0,00				
Total eligible costs				0,00	0,00	0,00	0,00	0,00	0,00	8 173,96	0,00	146 962,84	0,00	155 136,80	0,00	0,00	0,00	147 234,96	147 234,96
					0,00		0,00		0,00		8 173,96		146 962,84		155 136,80		0,00		
Maximum calculated EC contribution for the reporting period (in €) without taking into account receipts				0,00	0,00	0,00	0,00	0,00	0,00	8 173,96	0,00	139 061,00	0,00	147 234,96					
					0,00		0,00		0,00		8 173,96		139 061,00						
Amount of the financial interests generated by the prefinancing														0,00					
Requested EC contribution for the reporting period (in €)														147 234,96					

AUDIT CERTIFICATE

To

The Management of Institute of Applied Physics

59, Sankt Petersburg Blvd, Plovdiv 4000, pbox 823, Bulgaria

I, **Lyubka Trifonova Shumanska**, registered under N0077/2001 in the Register of Auditors at the Institute of Certified Public Accountants in Bulgaria, hereby certify that:

- I have conducted an audit relating to the cost declared in the Financial Statement per Activity of **Institute of Applied Physics,** hereinafter referred to as **contractor**, to which this audit certificate is attached, and which is to be presented to the Commission of the European Communities under **contract No 016805 (INCO) Specific Support Action** for the following period covered by the EC contract, **from 01.04.2005 to 30.09.2007.**

- I confirm that the audit was carried out in accordance with generally accepted auditing standards respecting ethical rules and on the basis of the relevant provisions of the above referenced contract and its annexes.

The above mentioned Financial Statement per Activity was examined and all tests of the supporting documentation and accounting records deemed necessary were carried out in order to obtain reasonable assurance that, in our opinion, based on our audit:

- the amount of the total eligible costs **EURO 155 136,80** (one hundred fifty fife thousand one hundred thirty six euros and eighty cents) declared in Box 2 on form C of the attached Financial Statement per Activity is complying with the following cumulative conditions:

    - ➢ they are actual and reflect the contractor's economic environment;
    - ➢ they are determined in accordance with the contractor's accounting principles;
    - ➢ they have been incurred during the periods covered by the Financial Statement per Activity concerned by this audit certificate;

- ➢ they are recorded in the accounts of the contractor at the date of the establishment of this audit certificate;
- ➢ they are exclusive of any non-eligible costs identified below which are established in the second paragraph of article II.19 of the above mentioned contract with the Commission of the European Communities:
  - any identifiable indirect taxes, including VAT or duties;
  - interest owed;
  - provisions for possible future losses or charges;
  - exchange losses;
  - costs declared, incurred or reimbursed in respect of another Community project;
  - return on capital;
  - debt and debt service charges;
  - excessive or reckless expenditure;
  - any cost which does not meet the conditions established in Article II.19.1. of your contract with the Commission of the European Communities.
- ➢ they have been claimed according to the following cost reporting model **"Full Cost with actual indirect costs (FC)"** which the contractor is eligible to use according to article II.22 of the above mentioned contract with the Commission of the European Communities;
- ➢ they are claimed according to the conversion rate of the date, where the actual costs were incurred. The basis for the conversion rate used of EURO is – 1,95583 leva:

- as declared in Box 3 of the attached Financial Statement per Activity, the total amount of receipts for the period covered by this Financial Statement per Activity is equal to 0 (zero) ;

- as declared in Box 4 of the attached Financial Statement per Activity, the total amount of interest yielded by the pre-financing received from the Commission of the European Communities for the period covered by this Financial Statement per Activity is equal to 0 (zero);

- accounting procedures used in the recording of eligible costs respect the accounting rules of Bulgaria and permit the direct reconciliation between the costs incurred for the implementation of the project covered by the EC contract and the overall statement of accounts relating to the contractor's overall business activity;

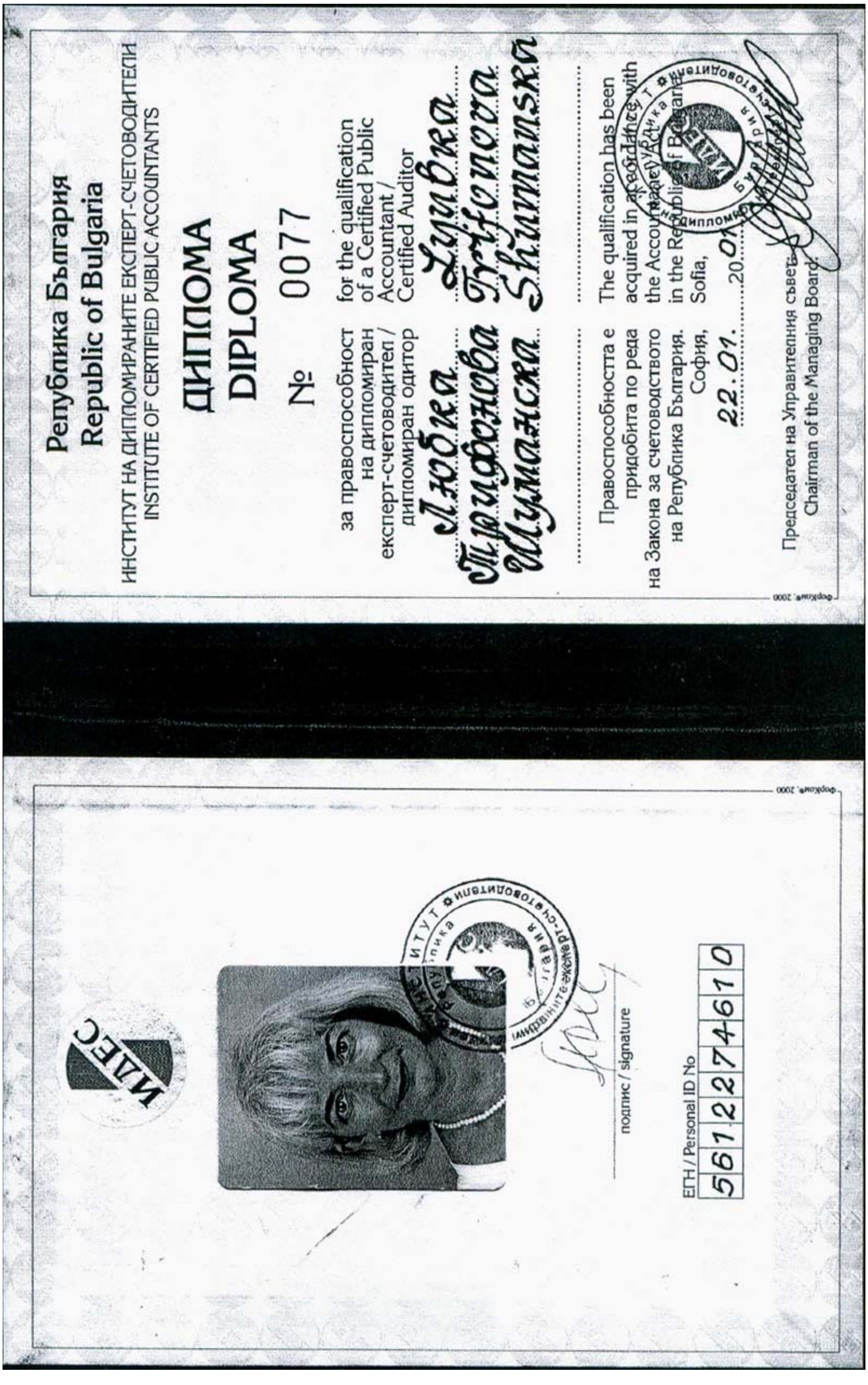
- I declare, that I am qualified to deliver this audit certificate in full compliance with the second and third paragraphs of article II.26 of the contract; (a copy of my license is attached to the this audit certificate)

30 October 2007

Lyubka Shumanska

Registered auditor

0077 Любка Шуманска
Регистриран одитор



Република България
Republic of Bulgaria

ИНСТИТУТ НА ДИПЛОМИРАНИТЕ ЕКСПЕРТ-СЧЕТОВОДИТЕЛИ
INSTITUTE OF CERTIFIED PUBLIC ACCOUNTANTS

ДИПЛОМА
DIPLOMA

№ 0077

за правоспособност на дипломиран експерт-счетоводител / дипломиран одитор

for the qualification of a Certified Public Accountant / Certified Auditor

Любка Трифонова Шиманска

Lyubka Trifonova Shimanska

Правоспособността е придобита по реда на Закона за счетоводството на Република България.

The qualification has been acquired in accordance with the Accountancy Act in the Republic of Bulgaria.

София, 22.01.20..

Sofia, 20..

Председател на Управителния съвет:
Chairman of the Managing Board:

подпис / signature

ЕГН / Personal ID No 5612274610