Synthesis Report

For Publication

Contract : BRE 2- CT92 -0292

Project: BE 5745

Title : Development of Industrial Low Temperature PVD Technique of Cubic Boron Nitride for Long Lifetime Products (LTcBN)

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References period: from 01/02/93 to 30/11/96

Starting date: February 1993 **Duration :** 47 months

Date of issue of this report : March 1997

Project funded by the European Community
under the Industrial & Materials Technologies
Programme (Brite-EuRam III)

Contents of the Synthesis Report

Keywords

c-BN, coating, sputtering, dc magnetron, tools

1 Abstract

Cubic boron nitride (c-BN) is a material well known for its chemical inertness and the excellent electrical, thermal and mechanical properties. Films prepared of c-BN will therefore have an enormous potential for many industrial applications.

This report deals with the successful preparation of cubic boron nitride (c-BN) films by use of the de-magnetron sputtering technique. Transfer methodes have been developed for c-BN process transfer between rf and dc magnetron driven laboratory sized systems as well as production plants. The dc process is based on the use of electrically conducting boron carbide (B_4C) targets.

The films showed excellent mechanical properties, e.g. hardness 60-80 GPa, very low wear resistance (1/ 10 compared to DLC) and a low friction coefficient (μ=0. 1 -0.2). For improvement of adhesion different interface systems have been investigated, prepared by means of the arc-bond-sputter technique (ABS). It turned out, that ABS improved film adhesion considerably, but it could be discovered within this work, that c-BN film delaminate on occurs cohesively within the BN film, possibly at the t-BN/c-BN interface. Additional research work has to be spent on this subject including ageing mechanism of c-BN films.

However, application oriented tests demonstrated the broad industrial potential of c-BN coatings. Drills coated with only 0.4 µm thick (c)-BN films withstood up to 50 holes drilled in CK45. Due to the low friction, the initial value of torque was only 75% of torque for TiN coated drills.

2 Consortium profile .

2.1 Partner organisations

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2.2 **Consortium description**

IST/FhG

The Institut für Schicht-und Oberflächentechnik (1ST) of the Fraunhofer-Gesellschaft (FhG), Munich, F.R.G. is a non-university institute founded in 1990.

The main goal of the 1ST is the development of new film systems and coating processes for the preparation of coatings for various applications. The scope of the institute covers a wide range of applications of thin films. Work on decorative coatings is carried out as well as applied research and development on coatings for electronic components, transducers, mechanical and chemical protection, optical applications and tribology.

Extended work has been carried out on the development of carbon-based layers and on investigations of their tribological, mechanical and electrical properties. Amorphous hydrogenated carbon films (a-C:H) and metal containing amorphous hydrocarbon films (Me-C:H) as well as thin cubic boron nitride (c-BN) films have been prepared by PVD and CVD methods at low substrate temperatures (< 300 “C). Extended research activities of the 1ST are related to the preparation of diamond films by different CVD methods. Moreover, the institute is active in the field of thin film analysis and thin film characterization with respect to structure and morphology as well as in mechanical, optical and electrical thin film characterizations.

Within the LTcBN project IST/FhG was responsible for the project coordination. Moreover, main tasks of this institute have been the development of a de-magnetron sputtering technique for c-BN coatings including the work on the selection of suitable targets. Work on very thin c-BN coatings for applications in the field of magnetic-tape components were performed as well as different approaches for the realisation of long-term stable and well adhering c-BN layers.

To this work was carried out by means of a flexible rf sputter device and transfer criteria have been developed. With respect to adhesion improvements different interface systems and arc-bonded interfaces were investigated. The work was covering different analytical and mechanical characterizations of the layers and the preparation of various samples for the project partners.

Hauzer Techno Coating Europa B.V.

Hauzer Techno Coatings Europe BV is a SME located in Venlo (The Netherlands). The company develops and manufactures sophisticated industrial coatings systems and processes, designed for PVD surface treatments. A strong effort is put into R&D of new deposition techniques, of new types of coatings and the industrialization of the obtained results. This has resulted in the development of new deposition techniques like the patented “Steered Arc Evaporation” and the patented “Arc Bonded Sputtering” deposition techniques.

The main tasks of Hauzer within this project have been a redesign of the boron containing target support and the optimization of the magnetron cathodes with respect to an increased ion density at the substrate holder. In particular support was given to the partners with respect to special ABS plant optimisations for c-BN growth. As a result of reorganisations of the work tasks of this project, Hauzer was responsible for arc investigations on different boron containing materials.

Günther & Co.

Günther & Co has more than 100 years experiences in the production and marketing of cutting tools, which are well known under the product name ‘Titex plus”. The turn over was in 1991 in the order of 100 Mio DM. The company is established in many European countries. Günther & Co. has own R&D activities. During the life time of this project the company became a subsidary of Sandvik.

The main tasks of Günther & Co within this project have been dedicated to **application** oriented tests of BN based coatings as prepared by other partners. To this Günther & Co has designed and manufactured special drills with different shapes and out of different base materials. The coated drills were tested at Gunther&Co in comparison to standard coatings and tools.

Philips Electronics N.V.

Philips Electronics N.V. parent company of Nederlandse Philips Bedrijven B.V. is known as a large producer of light and consumer electronic systems. In several factories worldwide recording systems are manufactured. In view of the fierce competition from the far-east, emphasis is on product innovation and improvements. Products of major importance are video and audio recorders and tapes.

Philips as the inventor of the audio cassettes holds several important patents in this field. In consequence of this , the company has an extensive experience in the development of all kind of tape recorders, heads and tapes.

The main tasks of Philips in the LTcBN project have been different analytical characterizations of the BN films, with special emphasis on structure and binding. To this the binding status of the residual carbon in the film was investigated as well as delamination zones of c-BN films on different substrates together with other partners. Moreover, various investigations have been carried out with respect to mechanical film characterizations especially on very thin c-BN films < 100 nm which were prepared on different substrates, including ceramic materials.

Linköping University

At the Department of Physics research concerning growth of thin films from the vapor phase has been conducted since 1973. The research is focused on understanding relationships between growth parameters, structures and physical properties of thin films. The goals of the research are both to increase the understanding of vapor phase growth and reactions in thin films on an atomistic level and to explore physical properties of structures unique to thin films. The research is relatively broad and covers several different material combinations and growth techniques.

The research program which is experimental in its character is focused on films grown by sputtering and evaporation techniques. The characterization of deposited films is concentrated onto structural techniques such as electron microscopy and x-ray diffraction. Physical properties are predominantly investigated in cooperation with other groups as described below. The emphasis is to understand kinetically limited growth processes and the program includes studies of; low-energy ion/surface interactions, growth on lattice-mismatched substrates, low-temperature growth, growth of superlattices, thin film solid phase reactions and sputtering of compounds (including nitrides, high-Tc superconductors and SiC).

The objectives for this programme were to increase the understanding of kinetically limited growth processes in combination with low-energy ion irradiation.

The main tasks of Linköping Univ. have been the characterization of c-BN coatings with respect to structure and composition, investigation of the substrate/c-BN interface due to morphology and in-depth characterization as well as investigations of the different interfaces as prepared by the project partners. Moreover, investigation of different BN coatings with respect to stress states of the coating/substrate combination, preferred orientation and dislocations. The most important tool for c-BN growth studies was the work on HRTEM and SAD, which means high resolution transmission electron microscopy and selected area diffraction.

3 Technical achievements

3.1 Introduction

Cubic boron nitride (c-BN) is an interesting material for many technological applications, because of its excellent physical and chemical properties. It has the second highest hardness next to diamond, a high thermal conductivity and a wide band gap [1]. An advantage of c-BN compared to diamond is the chemical inertness with respect to ferrous materials. Therefore c-BN is a promising coating material for an improved wear resistance of cutting tools.

At present commercially available c-BN tools me prepared as sintered material in a HPHT process [2]. In recent years several attemps were made to grow cubic BN films from the vapour phase at low pressures and low temperatures. Various PVD and PACVD methods have been developed to grow c-BN films. Typical PACVD methods in use are plasma assisted CVD [3] and ECR plasma CVD [4]. Important PVD methods for c-BN growth are ion plating [5], ion beam assisted deposition [6] and sputtering [7,8,14].

From the variety of deposition methods the sputter technique may have the highest potential for industrial applications. Conventional sputter arrangements in use are rf diode, rf magnetron and dc magnetron systems. Recently rf sputter techniques were succesful used for c-BN film preparation [7]. However, rf techniques are expensive and show low deposition rates. An alternative for industrial fabrication of coatings is de-magnetron sputtering, which is well established for different standard coatings.

Although a variety of different methods were used for c-BN preparation so far, non of these techniques were able to fabricate stable and adhering c-BN films.

In the present project we concentrated our work on the development of a novel process for the fabrication of c-BN coatings based on de-magnetron sputtering [8,14] and the arc bond sputter (ABS) technique [10,1 1]. ABS was used for the fabrication of different interfaces designed for a improvement of the BN film adhesion.

Since it was expected that the process window for c-BN coatings would be extremely small and the use of de-magnetron sputtering and ABS was completely unknown at project begin, we started this work with basic investigations on reactive rf sputtering of different target materials and the definition of transfer models to dc magnetron sputtering and finally to transfer an optimized c-BN sputter process to the Hauzer-HTC-1000-4 ABS production plant. To this considerable work was performed on an improvement of the different plants with respect to specific c-BN growth conditions and the construction of ABS targets.

Moreover, basic investigations have been carried out with respect to c-BN film growth in general, e.g. elemental composition, film structure, binding state and interface formation. The layers have been characterized due to their mechanical properties.

Application oriented goals of this project dealt on one hand with i) very thin films (50-100 nm) for wear protection in magnetic tape recording and on the other hand with ii) c-BN coatings for cutting tools (>1 µm). To this different test specimen and series of drills have been used.

3.2 **Experimental details**

The experimental work was performed by use of different sputter plants. Starting up activities were concentrated on rf-diode sputtering, alternative target selections and basic de-magnetron investigations, which have been carried out with a laboratory type equipment described in detail elsewere [13]. During this early investigations rf-bias was used at the substrates as well as dc bias. Based on this results a process transfer has been performed to industrial sized plants. For general investigations on de-magnetron sputtering of c-BN films a medium size plant with 0.5 m^3 chamber volume and two ubm-targets of about 300 cm^2 area was used [9]. The substrate arrangement was identical to the HTC batch coater. Arc investigations have been performed by means of the ABS technique, whereas interface investigations and tool coating experiments were performed by means of an industrial batch coater Hauzer HTC-1OOO ABS plant [12], which is shown schematically in Fig. 1. The plant has an octagonal geometry with a total chamber volume of lm^3. Base pressures of 2x10-6 mbar can be achieved by use of turbomolecular pumps. The plant was equipped with 4 cathodes of 600 x 190 mm^2. Each cathode can be used in unbalanced sputter or arc mode. The magnetic fields are arranged in a closed loop to increase the plasma density in the plant. The substrates can be heated by means of radiation heaters to temperatures about 550 “C.

B_4C, $TiB_2/BN/Al$, Ti and Cr targets were used for ABS and sputtering. TiB_2 and B_4C targets as well as a rnixtured target of TiB_2/BN have been basically investigated for arc processing.

The experimental work on a c-BN process development was carried out by use of a special circular substrate holder of 80 mm in diameter, which was placed stationary in front of a B_4C target. The distance was varied between 50 mm and 200 mm. For variations of the ion density at the substrate, a magnetic coil with 500 windings was installed behind the substrate holder, which was designed for in-situ integral and local ion density measurements at different bias voltages.

For monitoring the ion densities during ABS investigations on interfaces and BN sputter deposition, a special ion collector array was designed. This device as well as the redesigned version of the magnetically supported substrate table could be moved to the different targets. Thus Ti-B-N-C interfaces could be fabricated with gradients in composition and bias.

A different arrangement was used for investigations on arc bonded interfaces and for the coating of various test samples and series of drills. In this cases the 2 or 3 fold rotation of the standard substrate table was applied.

During these investigations only dc power was applied. The depositions have been performed in Ar or Ar/N_2 gas mixtures. We used Si(100) wafer, flat steel substrates, 100Cr6 plates, ceramic substrates (Al_2O_3-TiC) and different kind of drills as substrate materials.

For the coating of HSS and HM drills 3-fold rotation was used. The drills were wet-cleaned by application of tensidic bathes. Prior to deposition a well adapted ion cleaning process (sputter etching) or metal ion etching (arc based) was integrated into the subsequent preparation of interfaces and BN coatings.

The elemental composition of the deposited films was characterized by electron probe microanalysis (EPMA) and secondary ion mass spectroscopy (SIMS). The film structure with respect to the cubic phase was analyzed by infrared spectroscopy [JR), transmission electron microscopy (TEM) and with electron diffraction (ED). X-ray photoelectron spectroscopy (XPS) was applied for binding state analysis.

For mechanical characterization nanoindentation was used for hardness measurements and pin-on-disc testings for determining the friction behaviour. The wear resistance was detected by sphere-on-tape (SOT) tests. Scratch measurements were done to investigate the adhesion of the films. Although the c-BN coatings had a restricted thickness of $<0.5\,\mu m$, cutting tests on steel CK 45 have been performed by drilling.

3.3 **Target Materials**

Standard target materials in use for sputter deposition of boron nitride films are boron and hexagonal BN. However, these targets can be used only in rf plasmas due to their low electrical conductivity. As a result of extended investigations on alternative target materials, we found out, that boron carbide (B_4C) with an electrical conductivity of about 10^2 Ωcm can be used successfully for the fabrication of c-BN films by industrial dc magnetron sputtering techniques. Among other possible boron containing target materials B_4C has the advantage of forming volatile C-N molecules, e.g. C_2N_2, and thereby reduce the C-content in the as-depoited films.

Technical problems had to be solved by the preparation and bonding of extended boron carbide targets. The fabrication of monolithic targets with a size of 600 mm x 190 mm was not possible, because of the brittleness of boron carbide. Therefore novel targets consisting of up to 8 plates bonded to backing plates have been designed. As backing plate low expansion material e.g. Mo was selected successfully over stainless steel and copper.

3.4 Results and discussion

3.4.1 Investigation of reactive de-magnetron sputtering of B_4C

In order to develope dc magnetron sputtering for c-BN films, we frost had to deal with the adjustment of the elemental distribution in the reactively sputtered films. Figure 2 shows the distribution for the elements B,N and C as a function of the nitrogen flow by using Ar/N_2 gas mixtures $[N_2/Ar+N_2]$. The ratio B:N≈ 1 was obtained for nitrogen flows of >10%. Further additions of nitrogen led to a reduction of the carbon content in the films. Since the nitrogen content is also influencing the deposition rate, we choosed working conditions between 10 and 25% N,.

According to the literature [15,16,17] and to our previous investigations, c-BN growth was strongly dependent on ion interactions at the substrate. Thus specific investigations were carried out due to sputter gas composition, substrate bias potential and ion current density. Figure 3 shows the c-BN content in films sputtered from a boron carbide target, in terms of the infrared absorption ratio A_{cBN}/A_{hBN} and plotted against the nitrogen gas flow. It is important to mention, that N, additions of >50% led to instabilities of the dc plasma due to target poisoning.

Most important parameters for controlling the cubic phase of BN films are the energy and the current density of the ions, bombarding the substrate surface during the deposition. Figure 4 shows the influence of bias voltage variation on the cubic phase, whereas figure 5 defines the process window with respect to the ion current density. It can be taken from these results, that for obtaining the cubic phase, B:N ratios of close to 1 are a need together with the destinct adjustment of bias voltage and current density. For practical reasons process transfer criteria have been defined in terms of ion flux ϕ_i and deposited boron atoms ϕ_A which can be measured easily and were used for a threshold definition of the individual sputter plants.

Based on calculations of the actual deposited boron atoms the threshold of ions needed for c-BN formation described by the flux ratio ϕ_i/ϕ_A was for sputter depositions within the shown energy window in figure 4 ($\phi_i/\phi_A > 10$).

The structure of films fabricated by means of dc magnetron sputtering was comparable to rf sputtered c-BN films. Figure 6 and figure 7 shows examples of HRTEM images taken from layers deposited on Si-wafer. It turned out, that film growth occurs in three phases: i) an amorphous BN section of about 5 to 10 nm, ii) a textured turbostratic region and next to that iii) a nanocrystalline c-BN structure. The turbostratic interface was in the order of 20 to 50 nm. This growth structure has been observed on different substrates. Due to the energetic threshold discussed by figure 4, the t-BN interface could be extended by e.g. reduction of the substrate bias potential, but a variation of the sputter parameter discussed above, had little effect on minimisation of the a-BN/t-BN interface [18].

The interpretation of integral measurements of BN films by means of IR spectroscopy was difficult because of the structured interface. Thus IR absorption results on c-BN content in films do not show whether it was a mixtured h-BN/c-BN film or a sandwich-like structure of both phases with an almost single phase c-BN layer on top off the textured interface.

The binding of the residual carbon in the BN films has been investigated by XPS. Independent on sputtering conditions it was found, that BN films that are produced from a B_4C target only contain minor amount of phases with carbon - carbon bonds and/or entrapped nitrogen. Hydrogen has been measured in a few cases by ERD and SIMS. It was found that the hydrogen content at the Si/BN interface and at the sample surface is higher than in the bulk, where approximately 2 at% and 1 at% have been measured, respectively. Qualitatively this distribution has been observed also for oxygen measured by SIMS.

However, the status of c-BN film preparation allowed only the deposition of thin c-BN films < 0.5 p.m. Thicker films were not stable during sputtering and peeled of during the coating process.

3.4.2 **c-BN film fabrication by means of an industrial batch coater**

The aim of these investigations were the development of a c-BN process well adapted to standard industrial coating equipment and the fabrication of interfaces by an arc bonding technique. As discussed in the previous chapter, c-BN growth was effectively influenced by the intensity of bombarding ions and their energy in comparison to sputtered boron atoms. To this different measurements have been performed with respect to increasing the ion density at the substrates. Because of limitations due to target bonding the power at the B_4C targets was restricted to 6 W/cm^2. As shown in figure 8, up to 2 mA/cm^2 have been obtained under these conditions. Anyway, growth of cubic BN was not observed even at bias potentials between -200 and -300 V.

For determination of the specific process window of the ABS plant, measurements have been carried out be use of an internal focusing magnetic coil. Figure 9 shows the ion current density for different coil currents. It turned out, that the adjustment of both magnetic coils, the UBM coil and the internal coil, ion current densities up to 2.8 mA/cm^2 were measured. This led to a ratio of ϕ_i/ϕ_A in the range of 15 to 25 and c-BN growth was detected for bias potentials as low as -150 V.

Optimum working conditions for the static mode have been selected at a cathode power density of 5-6 W/cm^2, an argon/nitrogen gas mixture of about 20% (flow) and a substrate bias potential of -150 to -300 V. The substrate current density was tuned by the magnetic fields to about 2.4 mA/cm^2. The corresponding rate was in the order of 0.7 µm/h.

As a result of intensive process optimization, we finally found a set of parameters which enabled the growth of cBN layers without any internal coil. This was achived by carreful adjustment of the permanent magnets and the ubm fields of the cathodes.

The BN films prepared under these conditions showed an almost mono phase cubic structure as shown in figure 10, which shows the IR-absorption band of c-BN near 1100 cm-’ and of h-BN near 1400 cm-’ respectively 800 cm^{-1}. As characterized by HRTEM, IX-spectroscopy and nano-indentation, layers sputtered with the Hauzer-HTC 1000-4 ABS were comparable to films prepared by means of the above described plants.

3.4.3 **Investigation on ABS interfaces**

To improve the adhesion and stability of c-BN films investigations on different interface systems and bonding processes were carried out by ABS and sputter deposition. To this variations of the h-BN/c-BN interface were performed by varying the bias potential for increasing the h-BN interface. That lead to a remarkable improvement of the stabilisation of the c-BN films.

Investigations on ABS bonded interface systems were carried out in a semi stationary mode using Ti and Cr based interface systems for different substrates. This process was started in general with an arc metal-ion-etching step and the subsequent formation of gradient layers by variation of bias potential, reactive gas flow, temperature and process time. In comparison sputter ion assisted interfaces have been prepared with different gradients and thicknesses. These interfaces have been used as basis for c-BN layers which were fabricated continuously by moving the substrate table without interrupting the plasma from one cathode (e.g. Ti) to an other (B_4C).

For introducing boron containing interface systems directly to the substrate surface, investigations on arc processing of boron containing targets have been carried out. To this different conductive targets of TiB_2/BN, B_4C and TiB_2 have been investigated. Whereas TiB_2/BN and B_4C targets caused severe problems by arc treatment, good results have been obtained by use of TiB_2 cathodes. In this case ABS was performed at a current of 60 A at the TiB_2 cathode and bias values during etching and interface deposition of -1200 V and -100 V, respectively. SIMS results showed the presence of Ti and B on the etched samples with a penetration depth of some 10 nm , depending on the bias potential.

As a result of this project it turned out, that ABS bonded coatings showed an increased adhesion in comparison to sputter bonded layers. Scratch values for ABS and sputter-bonded films are compared in table 1. ABS bonded interfaces showed 100-120 N whereas sputter bonded showed only 40-45 N. TEM and SIMS investigation of interfaces showed that the ABS process will generate interfaces with penetration depth of some 10 nm. However, despite the excellent adhesion of the interfaces, the effect on the stability of c-BN films was only moderate.

SAM and EPMA measurements on delaminated c-BN films showed, that the fracture occurs within the BN film itself. Samples under investigation showed residues of BN on the substrate, resp. the interfaces. The fracture within the BN film, which might be discussed in terms of a cohesive failure mechanism, will possibly be caused by high internal stresses in the BN film. By using substrate bending methods, stress values were found between 2 and 6 GPa for c-BN films on Si-wafer. However, internal stresses at the phase boundaries between t-BN and c-BN might be much higher. Long-term storage experiments at reduced humidity showed, that c-BN film stability was influenced positively. Thus reactivity due to dangling bonds must be considered as source for film instability and delamination.

3.4.4 **Results on mechanical characterization**

With respect to various mechanical characterizations of the c-BN films it turned out, that c-BN showed very small friction coefficients as determined by pin-on-disc measurement. Depending on the surface topography friction coefficients for smooth films have been obtained in the range of 0.1 -0.2.

The hardness of high quality c-BN films as measured by nanoindentation was as high as 60-80 GPa.

For characterization of the abrasive wear resistance of very thin films, a special method developed by Philips was used. Sphere-on-tape (SOT) measurements were used to evaluate the wear resistance of the deposited c-BN layers. In this test a CrO_2 tape was moved over a coated sample with a sapphire sphere as load at the backside of the tape. The wear factor k is defined as $k=W/(F \cdot v \cdot t)$ with W the volume of the wear scar, F the normal force, v the tape velocity and t the running time. The results obtained by this method led to a first quantitative evaluation of the wear resistance of c-BN films.

Depending on the c-BN growth conditions wear factors have been determined to be as good as $0.05\ X10^{3}\,\mu m^3/J$. However, the results were not homogeneous and varied typically between 0.1 and $4\ X10^{3}\,\mu m^3/J$. A comparison of SOT results is given in table 2.

3.4.5 **Discussion of results on application oriented tests**

The c-BN layers prepared within this project have been evaluated with respect to applications on tools and magnetic heads. However, since Si wafers were used as standard substrate material due to IR transparency, the preparation of c-BN films on technical substrates had to be investigated at fret. As a result of this work it turned out, that the fabrication of c-BN films was possible by use of different substrates, like stainless steel, high speed steels, hard metal, molybdenum, copper or ceramic (Al_2O_3-TiC). The sputter parameter, however, had to be optimized. Adhesion and long term stability of films deposited on these substrates was in general a problem, but could be improved to some extend by variation of the ion cleaning and interface preparation conditions. Figure 11 shows as an example an IR spectrum taken in reflection from a c-BN film on HSS.

The application of c-BN films for wear protection on magnetic heads requires very thin films in the order of only some 10 nm. As substrate for this tests ceramic Al_2O_3-TiC samles were used besides Si wafers. Although c-BN layers could be prepared as thin films < 100 nrn with increased stability and goood adhesion on silicon, the yield on stabilized films on Al_2O_3-TiC ceramic was rather low. The main problem for wear protective layers on magnetic heads is, that the overall film thickness must be limited to about 50 nm or less. In case of c-BN film growth we always had to deal with an amorphous and textured turbostratic BN interface, which was in the order of 20-50 nm, depending on the sputter parameters.

As a result of these investigations it was concluded, that c-BN films with extended a-BN/t-BN interfaces are not a first choise for magnetic head application, although the cubic film material showed good wear properties.

Much better results in perspective have been obtained at application oriented tests on different drills, which have been performed at Gunther & Co. To this HSS and Hard Metal (HM) drills with different Ti-B-N and Ti-B-N-C/-hBN and cBN based layer systems were coated by use of the Hauzer batch Coater HTC-1OOO-4 ABS. It turned out, that the ion etching step prior to film deposition is very sensitive to erosion of the cutting edges of the drills. An improved treatment was developed at distinct ion energies. Adhesion as well as toughness of BN based films were improved further by heated substrates (>450 ‘C) prior to ion-etching and sputtering.

Moreover, field tests with different (c)-BN coated drills showed in tendency promising results. If we consider the small layer thickness of c-BN coatings of only 0.4 µm (thicker c-BN films were not stable and peeled of imidiatly), up to 50 holes have been drilled to steel C45. Results on HM coated drills showed promising results at wet cutting tests. By use of heat-coated (c)-BN drills up to 2600 holes have been drilled. It is important to note, that the initial value of torque was only 75% of torque for TiN coated drills.

3.5 **Summary and conclusion**

In conclusion the project was successful with respect to the development of an unbalanced dc-magnetron coating technique for c-BN layers. Based on the experimental work on a dc magnetron device we transfered the c-BN deposition process to a industrial sized ABS plant. Boron carbide was used as target material with a suitable electrical conductivity for dc sputtering. Considerable technical progress was done in the preparation and bonding of extended B_4C targets. By use of the ubm sputter mode we prepared single phase c-BN layers on ‘silicon, ceramic, hard metal and different steel substrates. The films showed excellent mechanical properties. The identification of the cubic phase was performed by IR-spectroscopy, transmission electron microscopy and electron diffraction. Sphere on tape measurements revealed a excellent wear resistance of the deposited layers.

ABS bonding led to a improved film adhesion, but it could be discovered within this work, that c-BN film delamination occurs within the BN film, possibly at the t-BN/h-BN interface. Additional research work has to be spent on this subject including ageing mechanism of c-BN films. However, application oriented tests as performed within this project, demonstrated the broad industrial potential of c-BN coatings.

4.0 Exploitation plans

In contrast to many other coatings, where an extensive development has led already to a sufficient know-how basis, the preparation of c-BN coatings is still at a very early stage. Especially in the field of low temperature PVD processing, the status of c-BN layer fabrication allowed not the preparation of c-BN films with a thickness >0.5 p.m. Moreover, to the preparation of c-BN coatings and their exploitation potential, we must consider, that

- the process is rather complex and needs high-fluxes of ions at the substrate
- the phase evolution will depend on a special interface system consisting of amorphous BN, highly oriented turbostratic BN and next to this c-BN. It should be a subject of further investigations whether the stability and delamination problem of c-BN films could be solved by interface modifications.

However, due to the still existing technological problems of c-BN coatings, industrial exploitation of the results of this project are not of short term character. Follow-up actions considered by the partners of this project will therefore focus on further development work on c-BN coatings in general, with strong application related optimization in the field of tool and mechanical component coating as well as the further development of industrial c-BN coating equipment.

Except one partner, the majority of the project consortium is heavily interested in follow-up actions dealing with the development of c-BN films related to the tool industry.

5.0 References

[1] J.H. Edgar, Properties of Group III Nitride, (Inspec, London, 1994)

[2] L. Vel, G. Demazeau, J. Etourneau, Mater.Sci. Eng. B1O (1991) 194

[3] M. Kuhr, S. Reinke, W. Kulisch, Surf. Coat. Technol. 74/75 (1995) 807

[4] M.J. Paisley, L.P. Bourget, R.F. Davis, Thin Solid Films, 235 (1993) 30

[5] M. Murakawa, S. Watanabe, Surf. Coat. Technol., 43/44 (1990) 128

[6] D.J. Kester, R. Messier, J. Appl. Phys. 72 (1992) 504

[7] M. Mieno, T. Yoshida, Surf. Coat. Technol., 52 (1992) 87

[8] A. Schütze, K. Bewilogua, H. Lüthje, S. Kouptsidis, Diam. and Rel. Mat. 5 (1996) 1130

[9] S. Koupsidis, H. Lüthje, K. Bewilogua, A. Schütze, P. Zhang, to be published in Diam. and Rel. Mat.

[10] W. D. Sproul, P.J. Rudnik, K.O. Legg, W.-D. Münz, I. Petrov, J.E. Greene, Surf. Coat. Technol. 56 (1993) 179

[11] W.-D. Miinz, F.J.M. Hauzer, D. Schulze, B. Buil, Surf. Coat. Technol. 49 (1991) 161

[12] W.-D. Münz, D. Schulze, F.J.M. Hauzer, Surf. Coat. Technol. 50 (1992) 169

[13] H. Lüthje, K. Bewilogua, S. Daaud, M. Johansson, L. Hultman, Thin Solid Films 257 (1995) 40

[14] M.P. Johansson, I. Ivanov, L. Hultman, E.P. Munger, A. Schütze, J. Vat. Sci. Technol. A 14(6) (1996) 3100

[15] S. Reinke, M. Kuhr, W. Kulisch, Diam. Rel. Mat. 3 (1994) 341

[16] D.J. Kester, R. Messier, J. Appl. Phys. 72 (1992) 504

[17] D.R. McKenzie, W.D. McFall, W.G. Sainty, C.A. Davis, R.E. Collins, Diam. Rel. Mat. 2 (1993) 970

[18] M.P. Johansson, L. Hultman, S. Daaud, K. Bewilogua, H. Lüthje, A. Schütze, S. Kouptsidis, G. S.A.M. Theunissen, Thin Solid Films 287 (1996) 193

Legends to figures and tables

Fig. 1: Schematic diagram of the Hauzer HTC-1OOO ABS plant

Fig. 2: Elemental distribution in the films as a function of the nitrogen flow by using Ar/N_2 gas mixtures

Fig. 3: Cubic phase content in films in terms of the infrared absorption ratio A_{cBN}/A_{hBN} plotted against the nitrogen gas flow (target power 1.5 kW, bias voltage -300 V)

Fig. 4: Cubic phase content in the films as a function of the bias voltage (target power 1.5 kW)

Fig. 5: Cubic phase content in the films as a function of the ion current density (target power 1.5 kW, bias voltage -300 V)

Fig. 6: Cross-sectional TEM image of the top surface and the substrate-to-film interface showing the typical nucleation sequence (a-BN => t-BN => c-BN) of a c-BN film

Fig. 7: Cross-sectional TEM image with a corresponding electron diffraction pattern in the middle region of a c-BN film

Fig. 8: Substrate current density as a function of the coil current for the system of four cathode coils without the use of the internal coil

Fig. 9: substrate current density as a function of the coil current for the internal coil, with and without the assistens of the system of four cathode coils

Fig. 10 : IR spectrum of a 0.3 μm thick c-BN layer

Fig. 11 : IR spectra taken in reflecion from a c-BN film on HSS.

Table 1 : c-BN deposition parameters Scratch results on deposited steel samples with and without arc interlayers

Table 2: Wear factor k of c-BN films in compare to other measured coatings

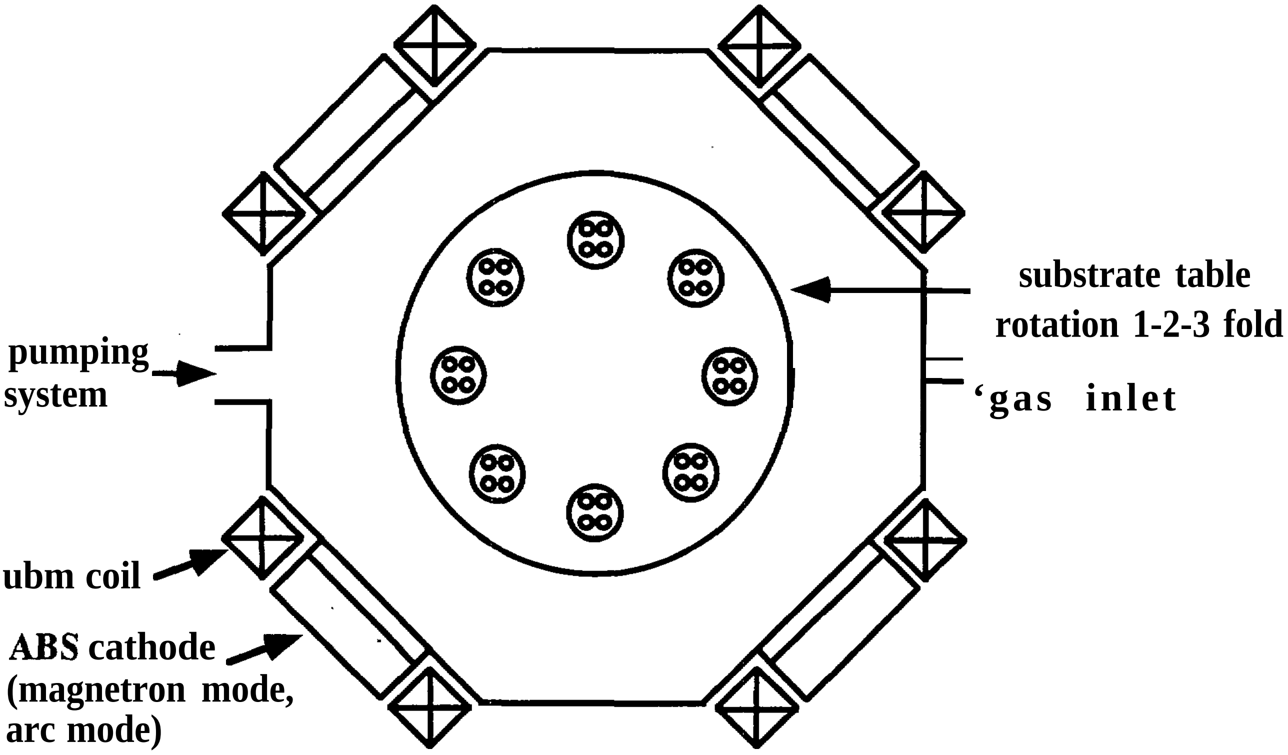

substrate table
rotation 1-2-3 fold
pumping
system
'gas inlet
ubm coil
ABS cathode
(magnetron mode,
arc mode)

Fig. 1

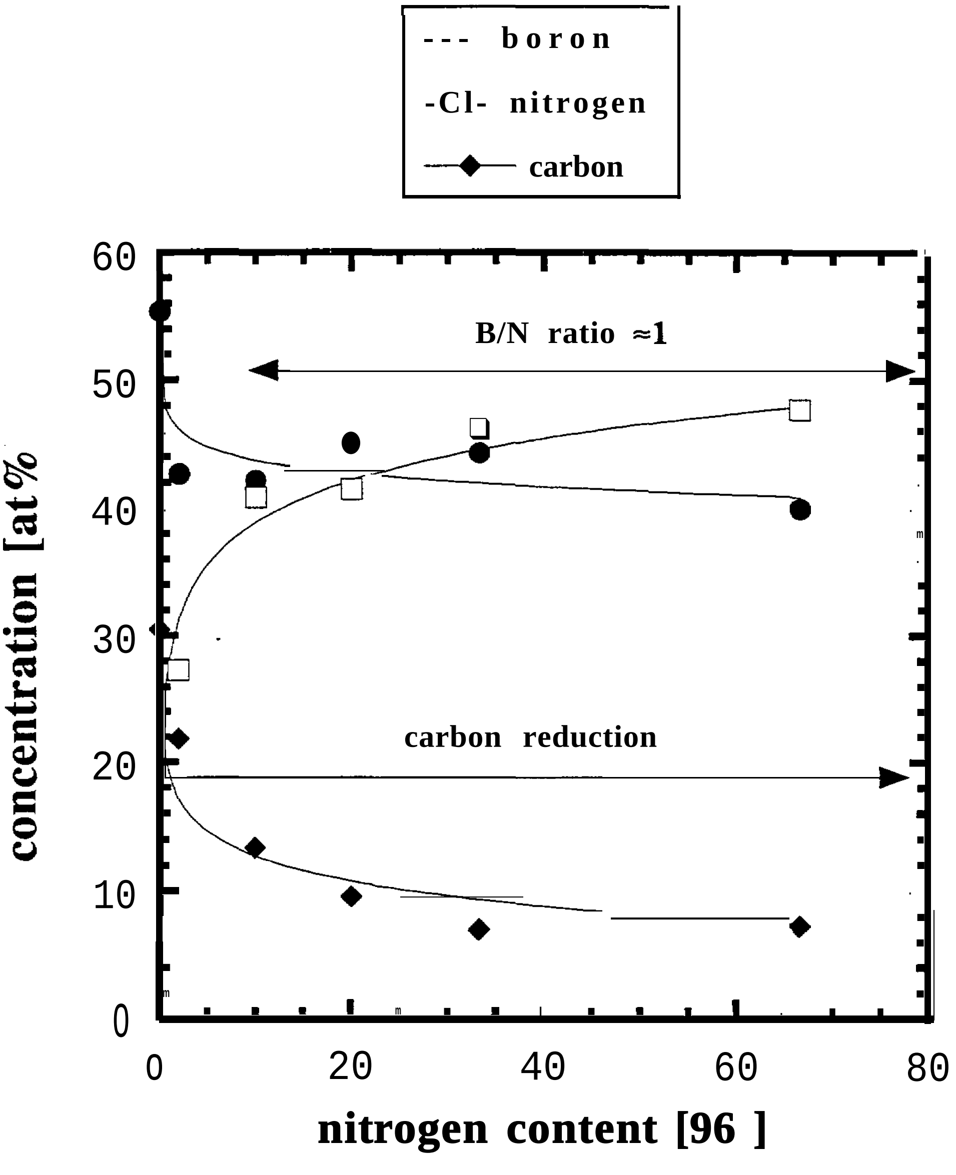
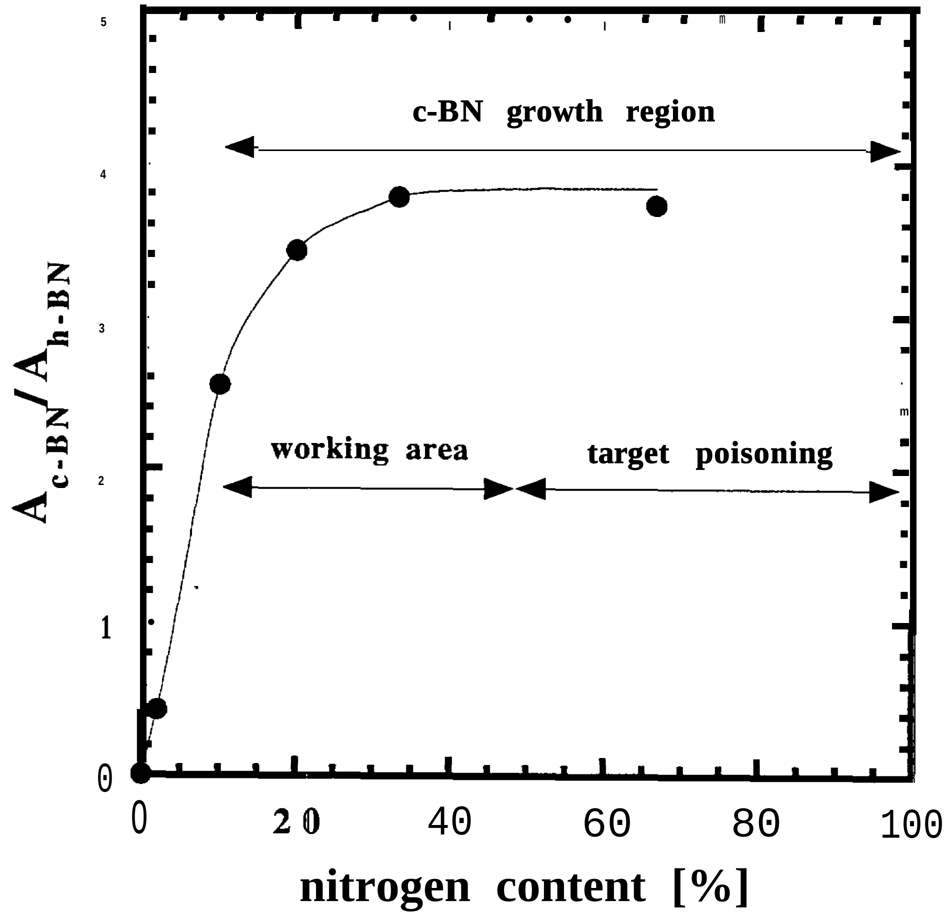
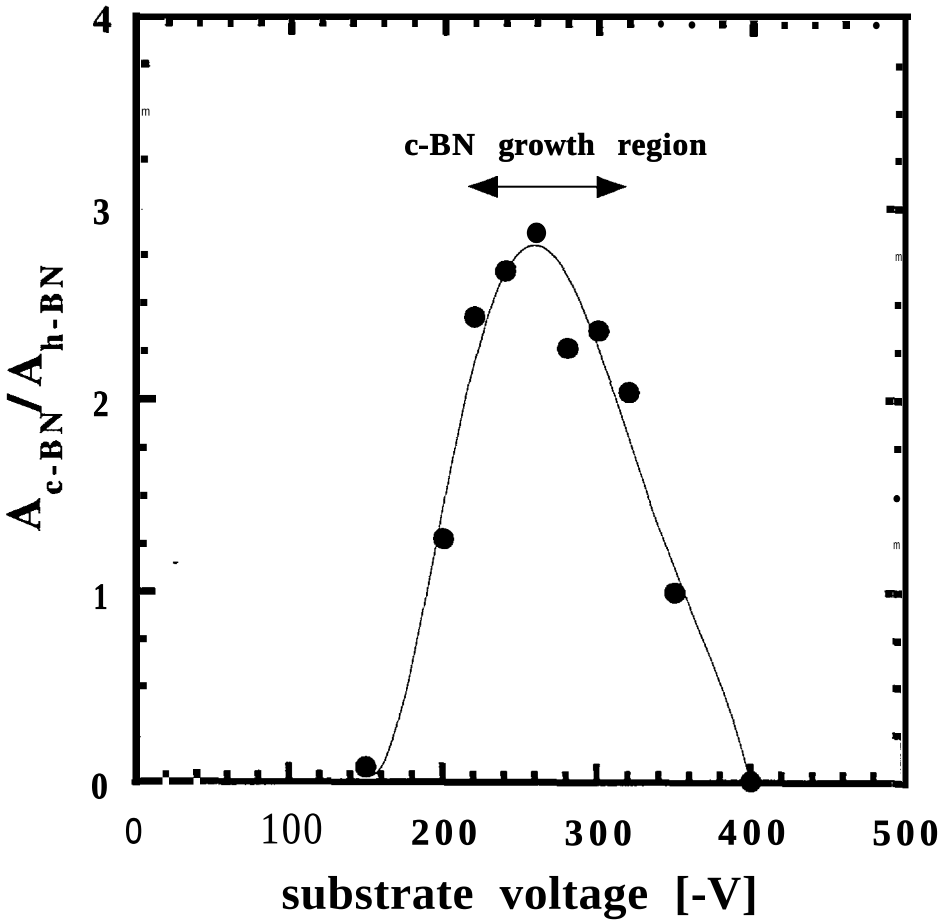

--- boron
-Cl- nitrogen
carbon
B/N ratio ≈1
carbon reduction
concentration [at%
0
10
20
30
40
50
60
0
20
40
60
80
nitrogen content [96]

Fig. 2



c-BN growth region
working area
target poisoning
$A_{c\text{-}BN}/A_{h\text{-}BN}$
0
1
2
3
4
5
0
20
40
60
80
100
nitrogen content [%]

Fig. 3



c-BN growth region
$A_{c\text{-}BN}/A_{h\text{-}BN}$
0
1
2
3
4
0
100
200
300
400
500
substrate voltage [-V]

Fig. 4

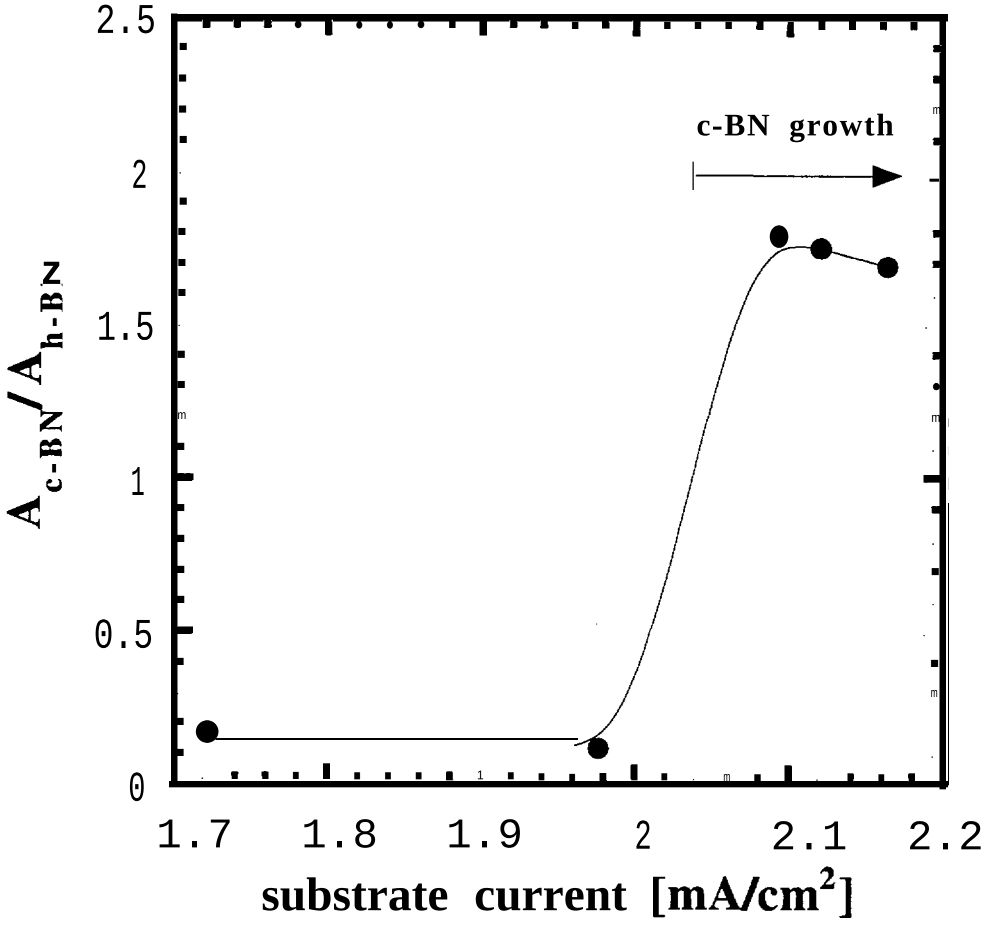

2.5
2
1.5
1
0.5
0
$A_{c\text{-}BN}/A_{h\text{-}BN}$
c-BN growth
1.7
1.8
1.9
2
2.1
2.2
substrate current [mA/cm^2]

Fig. 5

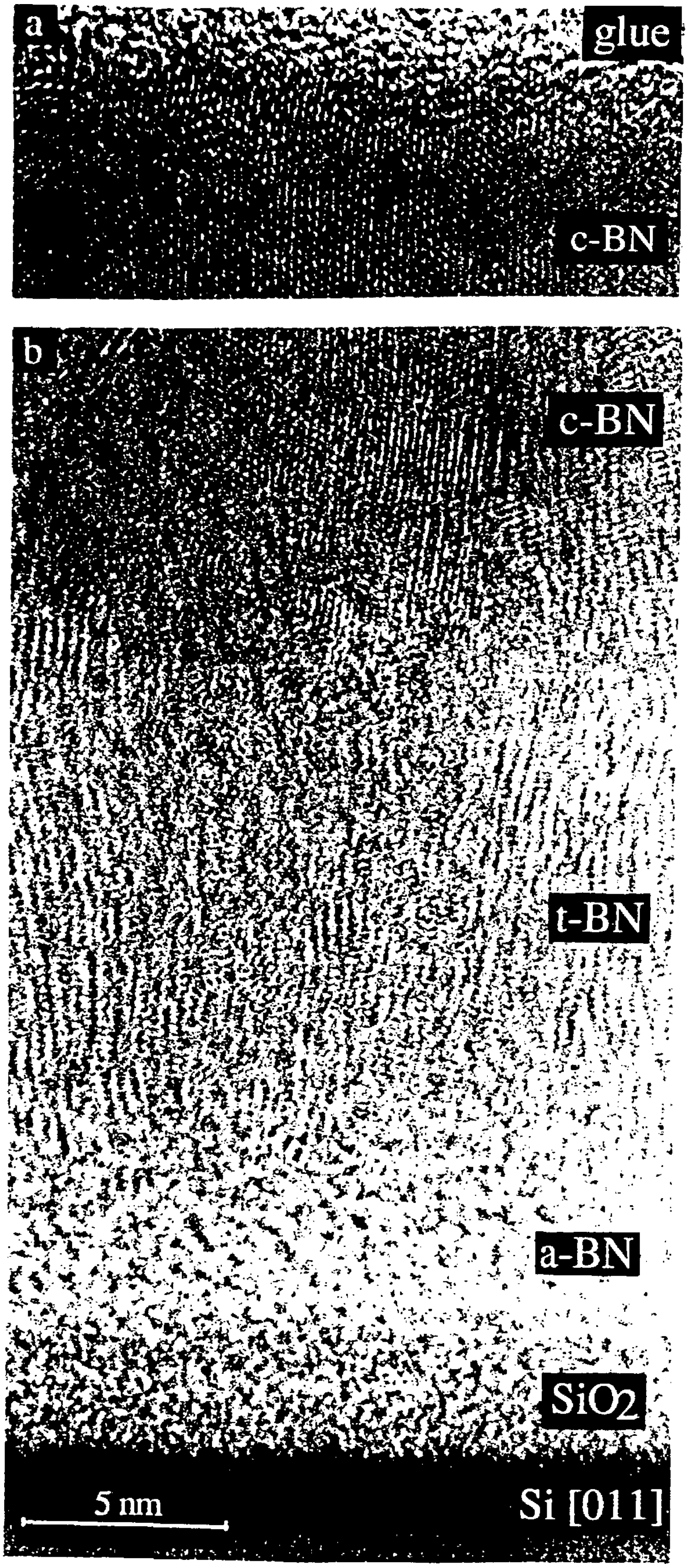


Fig. 6

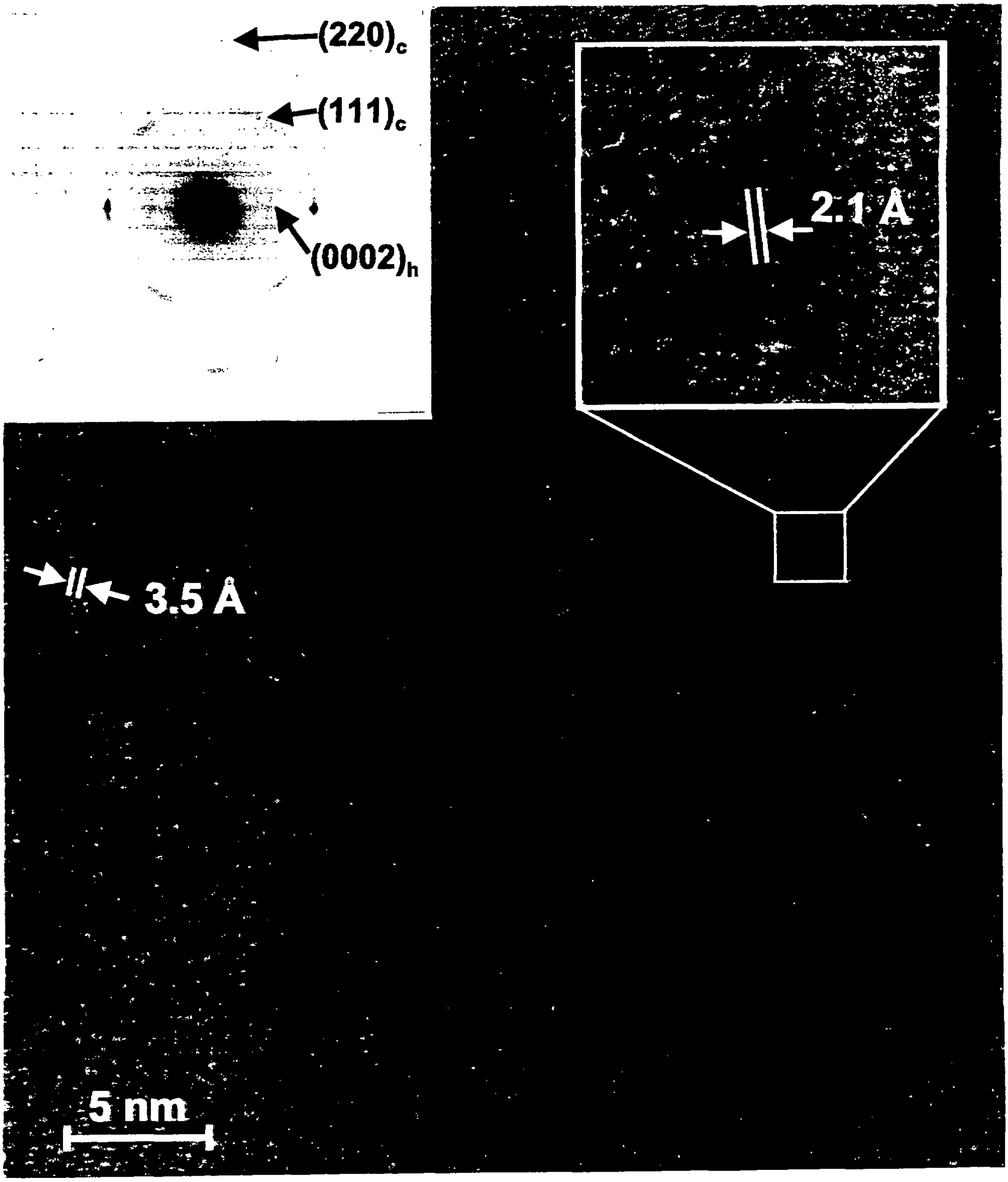


Fig. 7

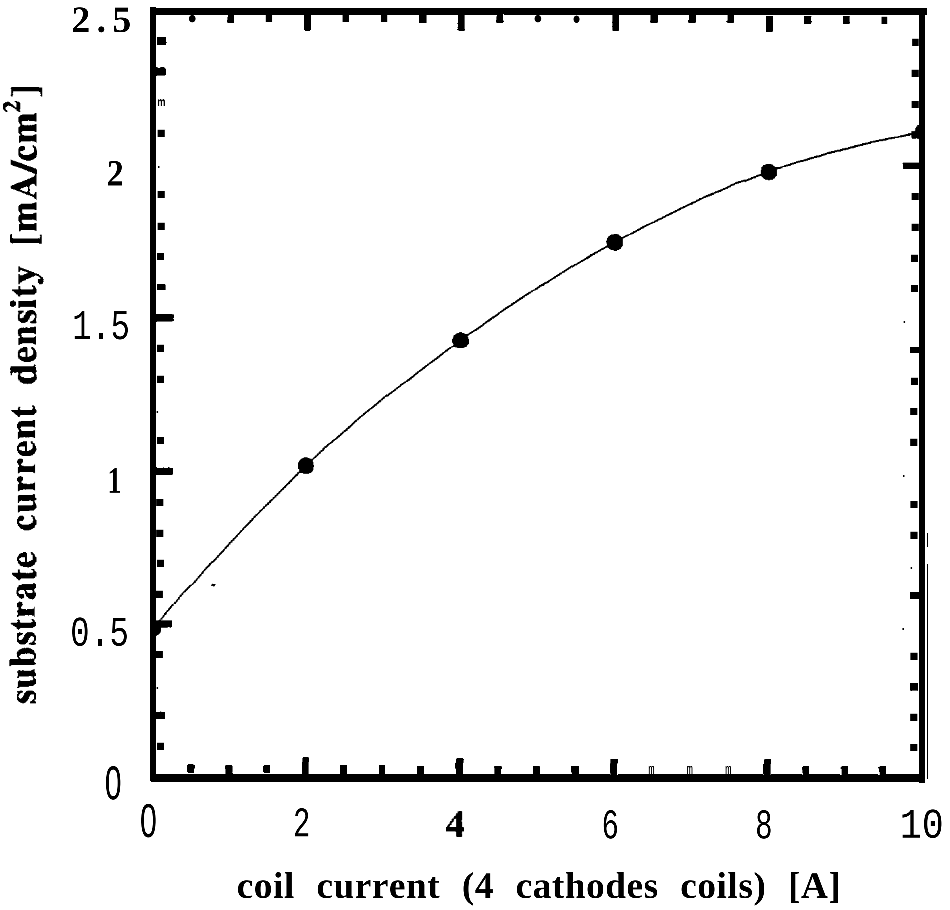
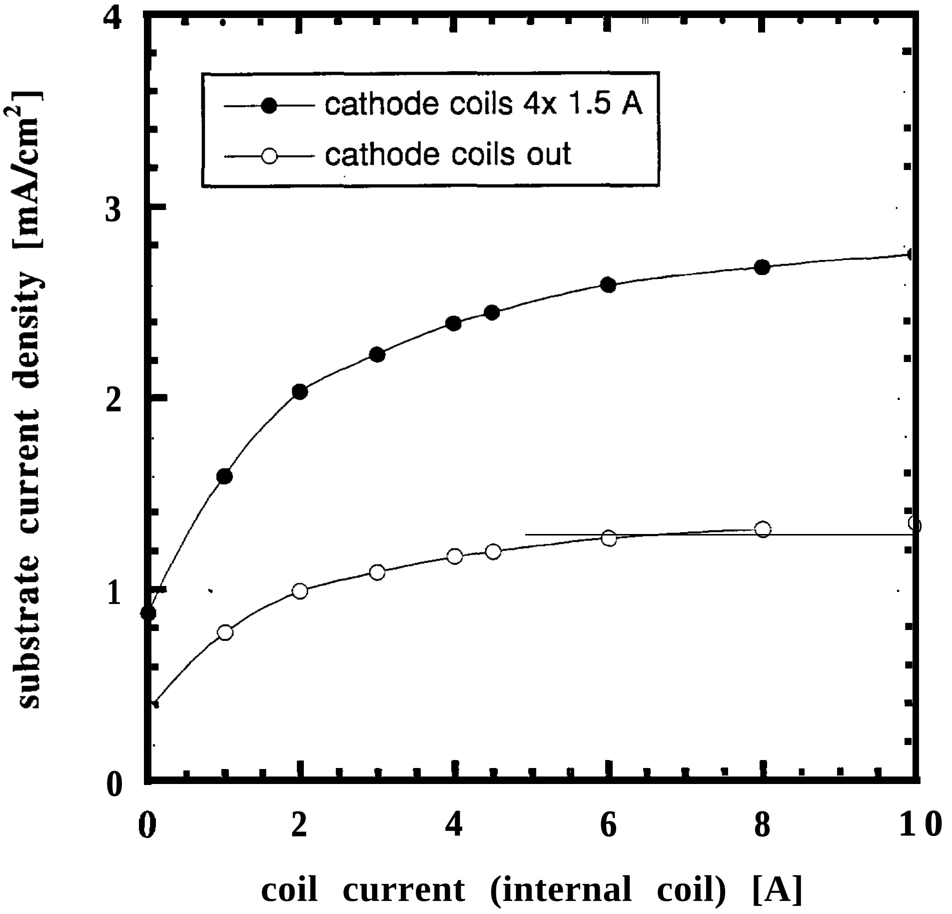

2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
substrate current density [mA/cm^2]
coil current (4 cathodes coils) [A]

Fig. 8



substrate current density [mA/cm²]
coil current (internal coil) [A]
cathode coils 4x 1.5 A
cathode coils out
0
1
2
3
4
0
2
4
6
8
10

Fig. 9

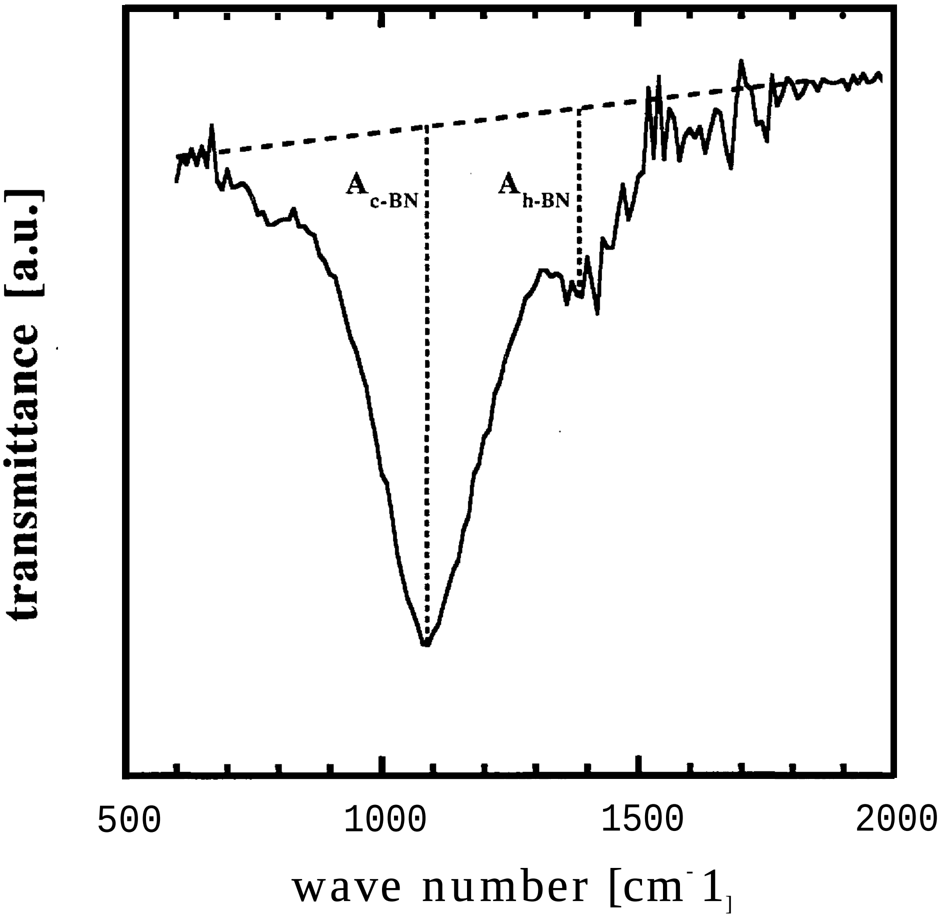
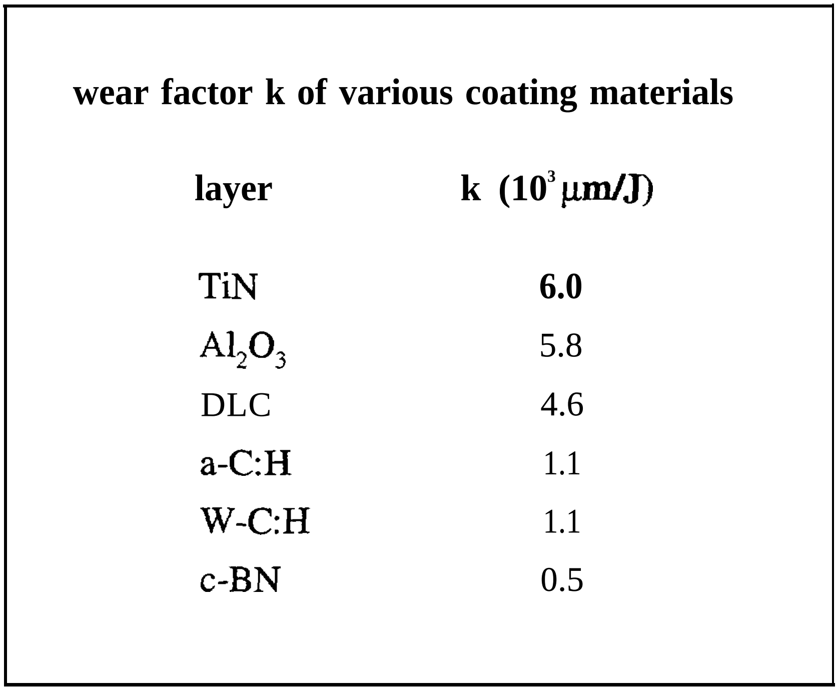

transmittance [a.u.]
A c-BN
A h-BN
500
1000
1500
2000
wave number [cm-1]

Fig. 10

scratch testing of coated steel samples

sample	interlayer	critical load N]
HSS	ion-etched	40-45
HSS	abs-prepared	95-1oo

Table 1



wear factor k of various coating materials

layer	k (10^3 µm/J)
TiN	**6.0**
Al_2O_3	5.8
DLC	4.6
a-C:H	1.1
W-C:H	1.1
c-BN	0.5

Table 2