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MAGNETRONIC DEPOSITION OF POLYCRYSTALLINE LAYERS OF TiN_x

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ABSTRACT

The present paper deals with the problems of deposition of hard, abrasion-resistant layers of TiN_x by the method of magnetronic sputtering using planar magnetrons. The basic principles of the apparatus and method used in the actual deposition process, control of the working atmosphere suitable for the creation of layers are reported, and the results of standard cutting tests described. The results show that the composition of the layer has a considerable effect on the performance properties of the respective tool, as well as on the physical properties of the layers.

1. INTRODUCTION

In recent years, significant developments have been achieved in the field of physical deposition methods used to apply thin abrasion-resistant layers of titanium nitride in vacuum. The methods in commercial use are based on the principle of vaporizing titanium by means of an electron beam (e.g. TINA 900 - East Germany or BAI 830 Balzers, Liechtenstein), by means of a low voltage arc (Bulat 3T, NNV 6 - USSR or NNO 150 ZEZ Prague) or on apparatus sputtering or vaporizing and depositing titanium by means of planar magnetrons.

The method of magnetronic deposition of thin layers in vacuo is multi-purpose, i.e. its use for deposition of TiN_x is just one of its many application possibilities. At the Research and Development Centre of ZEZ in Liberec, experiments are under way on the Z 700 apparatus by Leybold AG; some properties of TiN_x polycrystalline layers deposited by means of magnetrons are studied and the actual deposition method is verified. Some of the results of these investigations are described in the present paper.

2. DESCRIPTION OF THE APPARATUS

The apparatus shown in Fig. 1 consists of vacuum chamber 1, a pumping system comprising a rotary two-stage oil vacuum pump 2, Roots' vacuum pump 3 and

and turbomolecular vacuum pumps 4. The limit residual atmosphere in the chamber corresponds to 1×10^{-4} Pa. The apparatus is provided with a system of mass flowrate meters 5 for metering the doses of working gases.

The working atmosphere is monitored by the PGA 100 mass spectrometer 6 having its own pumping system 7 with a turbomolecular vacuum pump. The total pressure of residual gases is measured by thermoelectric and Penning's vacuum gauges. The total pressure during the introduction of working gases is measured by ionization vacuum gauge 9.

The apparatus is fitted with four magnetron cathodes PK 500 having indirectly water-cooled targets 488 x 88 mm in size. The magnetic fields of the magnetrons can be shifted. The magnetrons are placed in pairs facing each other with the targets 120 mm apart and supplied by SSV 15 sources 10 at a maximum voltage of 650 V and a maximum current of 15 A. For ionic cleaning of the substrate, the apparatus is equipped with a max. 2 kV source 12. For the bias during deposition, the source 13 provides the maximum working voltage of 350 V.

3. PRINCIPLE OF THE METHOD

The principle of the method is based on glow discharge, created around the cathode (of the material being sputtered) by high negative voltage. In the dark space of the cathode, ions of an inert gas such as argon, are accelerated towards the cathode where they interact with the target surface as a result of their high kinetic energy, and bring about so-called sputtering of atoms from the cathode surface.[1] If a magnetic field is created below the cathode and has a shape allowing the drift of emitted secondary electrons in directions $\overline{E} \times \overline{B}$ to become a closed circuit, the ionizing efficiency of the process becomes considerably enhanced as a result of extending the ionizing path of the electrons. The secondary electrons do not escape from the discharge space, being retained there by Lorentz's force.[2] They perform a cycloidal motion and during their retention in the magnetic tunnel hit the neutral argon particles and the sputtered target atoms, ionizing them in the process.

Figure 2 shows a schematic diagram of a couple of sputtering magnetrons. The electric field of the cathode is represented by vector $\overline{E}$ and the magnetic field by the magnetic induction vector $\overline{B}$. Magnetic circuit 1 is formed

by a system of permanent magnets and placed on a plate of ferromagnetic material 2. The target of the material being sputtered 3 is situated on the cooling plate of the magnetron body 4 and exposed to the incidence of the argon ions. The electrons are accelerated in the electric field of the cathode and the higher their velocity, the greater the effect of the magnetic field on their motion in the magnetic tunnel.

If their velocity decreases as a result of the collisions, the fast electrons become slow and escape towards the anode owing to the weak effect of the magnetic field.

A region of plasma with a high content of ionized particles is formed in front of the cathode as a result of the higher efficiency of the ionization process. If the magnetron cathodes are placed one against the other, the plasma regions of both cathodes combine and create favourable conditions for deposition of layers onto rounded substrates at suitable temperatures. The deposition rates achieved by the individual cathodes even show superposition.

The processes taking place in front of the cathode are influenced by the material of the target and its sputtering characteristics, the electric output at the cathode, the intensity and distribution of the magnetic field, the total pressure and the partial pressures of the reactive gases, the negative bias on the substrate, etc. The system involved is therefore very complex, but its optimization allows hard, abrasion-resistant layers of TiN_x to be deposited onto metal substrates at temperatures between 300 and 500°C.

4. WORKING ATMOSPHERE

Optimum control of the working atmosphere for the reactive process of depositing thin layers of TiN_x by means of planar magnetrons is one of the basic conditions of the deposition process.

Figure 3 shows the relationship between the deposition rate and the partial pressure of nitrogen as the reactive gas. The highest deposition rate is achieved in the deposition of metallic Ti. The deposition rate decreases with increasing nitrogen flowrate, reaching a minimum at a certain flowrate of the reactive gas. This phenomenon is associated with deposition of TiN_x compounds onto the titanium target in regions with a lower intensity

of the magnetic field. A diagram of experimentally established p_{N_2} values vs. the nitrogen flowrate for one, and for four magnetron cathodes PK 500 is plotted in Fig. 4. The dependence indicates that during the first stage, the consumption of nitrogen increases with its flowrate. This is due to the reaction with Ti as well as to sorption effects. When the nitrogen flowrate is further increased, a layer of TiN_x begins to deposit in the neighbourhood of the main erosion region, and the sputtering efficiency of the magnetron decreases, as does the consumption of nitrogen. Its partial pressure rises sharply and the deposition on the target becomes even more intensive. The deposition rate falls to 20% of its original value.

When the nitrogen flowrate falls, the state of the target is not regenerated, and so the partial pressure will decrease almost linearly with this decreasing rate. The so-called hysteresis effect occurs, its extent depending on various parameters, but above all on the pumping rate of the vacuum pump system. The higher the rate, the smaller the hysteresis effect. If the pumping rate of the system exceeds the critical rate, hysteresis will not take place at all.[3]

If the deposition rate is to be maintained at the maximum value, the reactive gas flowrate should be kept within the transition region as close as possible to point A. When the pumping rate of the vacuum system is sufficiently high and stable, the partial nitrogen pressure can only be controlled by controlling the rate of decrease in terms of the mass of the gas. However, the condensing area of the substrate must be kept constant, according to an additional precondition. If this requirement cannot be met, it is advantageous to control the partial nitrogen pressure. The account given above also indicates that the state of the target surface should be regenerated prior to each subsequent deposition cycle by its extensive sputtering in a non-reactive medium, in order to ensure a satisfactory reproducibility of the processes.

5. THE PROPERTIES OF TiN_x LAYERS

With magnetron deposition of the TiN_x layers, the latters' properties can be influenced over a wide range of values. This is mainly because it is possible to create layers with a wide range of stoichiometric ratios $x = N/Ti$. Figure 5 shows a typical dependence of the microhardness of TiN_x layes on the nitrogen flowrate. The dependence exhibits a sharp peak approximately in the region of stoichiometry. Figure 6 shows a plot

of the chemical composition of the TiN_x layer vs. the nitrogen flowrate. The dependence was established by means of Auger electron spectroscopy and the x = N/Ti value was determined from the deviations at primary beam energies of 382 and 420 eV, respectively. The dependence indicates that at low nitrogen flowrates, the layer is composed of an interstitial solid solution of nitrogen in α-Ti. Increasing the nitrogen flowrate produces only layers of polycrystalline δ-TiN. With this deposition method, the ε-Ti_2N phase is only formed under exceptional conditions.[4]

The TiN_x layer is mildly above-stoichiometric over a considerable range of nitrogen flowrates. This is very probably due to vacancies at the titanium points in the basic structural lattice of δ-TiN. As indicated by the recent results reported by Hultman[5], the bubbles of N_2 built into the layer during deposition and molecular in size may also have an effect on the non-stoichiometry of the layer. The TiN_x layers for engineering applications have the range $x = N/Ti \geq 1$. Their performance properties are therefore affected not so much by the chemical composition, but rather more by their physical properties, above all by the layer structure and morphology, orientation and size of its crystallites and the inner macroscopic and microscopic stresses in the layer.

Figure 7 shows a plot of texture coefficient TK vs. the reactive gas flowrate at U_B = -150 V. Figure 8 represents the dependence of TK_{111} on the bias on the substrate in the course of deposition, and Fig. 9 the dependence of TK_{111} on ion current at the substrate. The three quantities are of decisive significance for controlling the orientation of crystallites in the layer.

The preferred orientation of crystallites occurs in direction 111. This texture depends proportionally on bias, but decreases with an increasing value of ion current acting on the substrate. In our case, its value was varied by means of the current output of the magnetron, while keeping a constant input of 10 W cm^{-2} acting on the substrate.

The inner macroscopic stress is influenced by similar process parameters. The stress arises as a result of the different thermal expansions of the layer and the substrate, as well as of the negative bias on the substrate. Figure 10 demonstrates the difference in lattice parameters of the compact

layer on the substrate and those of a chemically separated layer, measured by means of X-ray diffraction. The dependence indicates maximum values of macroscopic stress in the region of maximum layer hardness, and shows that the compressive stress values grow with increasing bias.

The dependence of the difference in lattice parameters Δa on bias U_B is plotted in Fig. 11. At values of $U_B < 60$ V, tensile stresses arise in the layer and decrease gradually, while at $U_B > 60$ V, the stresses are compressive in character. The maximum values of macroscopic stress are attained at $U_B = -250$ V. The dependence shows that with a suitably chosen bias it is possible to create polycrystalline layers of TiN_x with zero inner stress. The values of compressive stress measured from the difference in lattice parameters of the layers before and after their separation are considerable and exceed the cohesion strength of the substrate. This fact has not been so far explained. Figure 12 is a plot of lattice parameters of compact and separated layers vs. the current output of the magnetrons. The relationship indicates that the inner stress in the layer decreases with increasing ion current, similarly to its texturability in the previous case. The above dependences show that the optimum conditions for deposition of TiN_x will lie in that region where minimum macroscopic stresses in the layer are attained.

6. PERFORMANCE PROPERTIES OF TiN_x LAYERS

A satisfactory adhesion of TiN_x layers to the substrate is a basic prerequisite for full utilization of their performance properties. The dependence of adhesive force on the nitrogen flowrate, measured by the scratch test method, is plotted in Fig. 13. The lowest adhesion values were attained with layers showing the maximum microhardness values, and thus also the maximum inner stress. However, the decisive criterion for performance properties of the layers is given by cutting tests which allow the layers to be evaluated in a complex way. Figure 14 shows the dependence of the number of drilled holes for 6 mm dia. drills provided with a deposited layer of TiN_x applied at various nitrogen flowrates. The dependence was measured at a tool feed of $s = 0.07$ mm/rev. The number of holes drilled with the Ti-coated tool was practically zero. The durability of the cutting edge of the tool increased only when the nitrogen flowrate exceeded 30 ml min^{-1}. The maximum was attained at a nitrogen flowrate above 45 ml min^{-1} and the value remained virtually the same at increasing flowrates.

The same dependence, but for s = 0.14 mm/rev., is plotted in Fig. 15. At low nitrogen flowrates, the course of the dependence is similar to that in the previous case. However, when the nitrogen flowrate is further increased, the dependence exhibits an outstanding peak at 50 ml min^{-1}. This point therefore corresponds to the optimum conditions for deposition, where the layers have the best performance properties and also a high resistance to oxidation at high temperatures. The latter is of decisive significance for correct performance of the layer even under the most difficult cutting conditions. At a nitrogen flowrate of 50 ml min^{-1}, the resulting layer therefore exhibits the highest stability. X-ray examination also indicates a minimum inner stresses for this region, as shown by the expanded diffraction lines for microscopic stresses, and by Fig. 10 for the macroscopic ones. The TK_{111} textural coefficient here reaches its maximum values, and orientation of crystallites in directions 200 and 220 is almost completely suppressed.

7. CONCLUSIONS

Deposition of polycrystalline TiN_x layers by means of planar magnetrons is a method that allows layers with very variable properties to be created. The properties depend on many deposition parameters, but primarily on the temperature of the substrate, on the partial nitrogen pressure, on the current of ions acting on the substrate and on the deposition bias.

In view of the fact that the range of optimum conditions for deposition is very narrow and shows a great spatial dependence, this method of treating cutting tools is highly demanding with respect to maintaining these parameters and controlling them within the optimum limits.

The method has the advantage of allowing for atomic sputtering of a layer without the presence of any macroparticles, of permitting a great variability in the properties of the layers to be achieved, including their colour which is particularly important for decorative applications, as well as of providing the possibility of depositing layers of non-standard composites consisting of various metallic elements regardless of their vaporization temperatures.

It may therefore be concluded that the method of reactive magnetronic deposition of abrasion-resistant layers is highly promising even in the future, and

that there is a number of commercial applications where its utilization must necessarily be given the top priority it deserves.

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5. L.HULTMAN: Growth of single and polycrystalline TiN and ZrN thin films by reactive sputtering: influence of low energy ion irradiation. Dissertation No.186, 1988, Linkoping.

FIGURE CAPTIONS

Fig. 1 Schematic diagram of the Z 700 apparatus by Leybold AG 1 - Vacuum chamber, 2 - rotary vacuum pump, 3 - Roots' vacuum pump, 4 - turbomolecular vacuum pump, 5 - mass flowmeters, 6 - measuring chamber of the mass spectrometer, 7 - pumping system of the mass spectrometer, 8 - measuring the total pressure of the residual atmosphere, 9 - measuring the total pressure of the working atmosphere, 10 - magnetron supply sources, 11 - source for ionic cleaning of the substrate, 12 - bias source for deposition.

Fig. 2 Schematic representation of a pair of sputtering magnetrons 1 - magnetic circuit, 2 - plate of ferromagnetic material, 3 - sputtering target, 4 - magnetron body with cooling ducts

Fig. 3 Deposition rate of TiN_x layers vs. reactive gas flowrate.

Fig. 4 Partial nitrogen pressure vs. reactive gas flowrate without the magnetrons, with one and four PK 500 magnetron cathodes, respectively.

Fig. 5 Microhardness of TiN_x layers vs. reactive gas flowrate.

Fig. 6 Stoichiometric ratio of TiN_x layers vs. reactive gas flowrate evaluated by means of Auger electron spectroscopy.

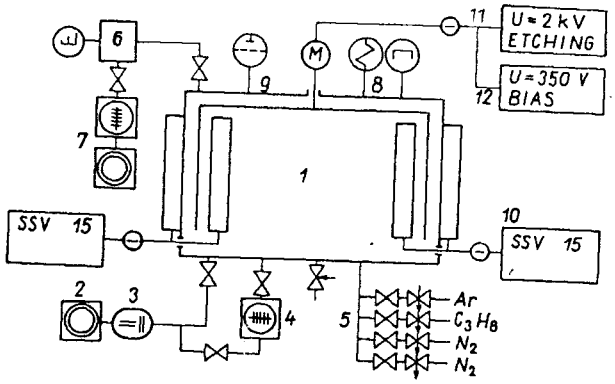

Fig. 1

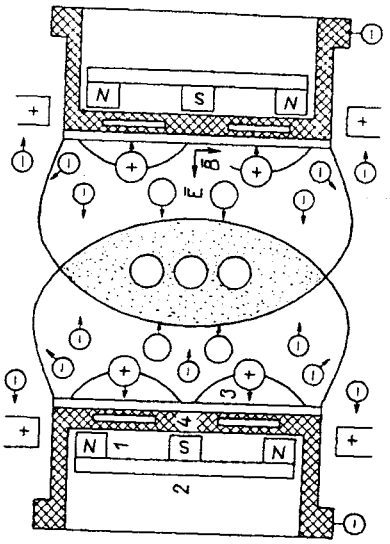

Fig. 2

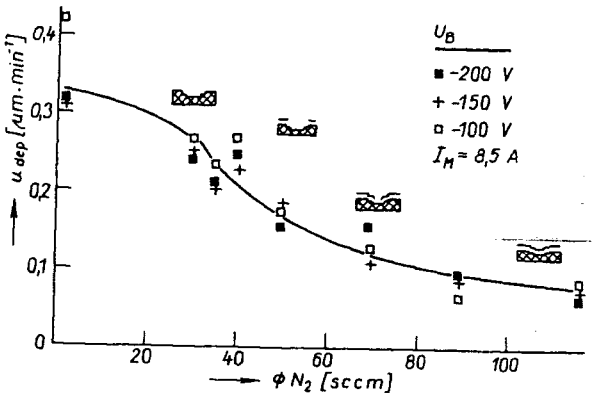

Fig. 3

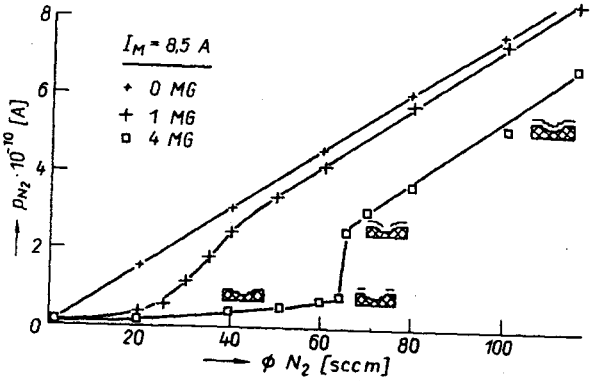

Fig. 4

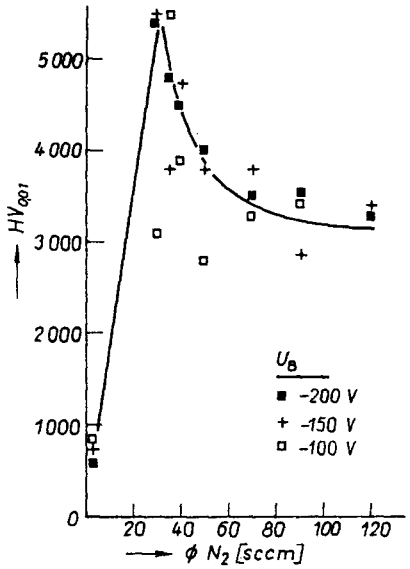

Fig. 5

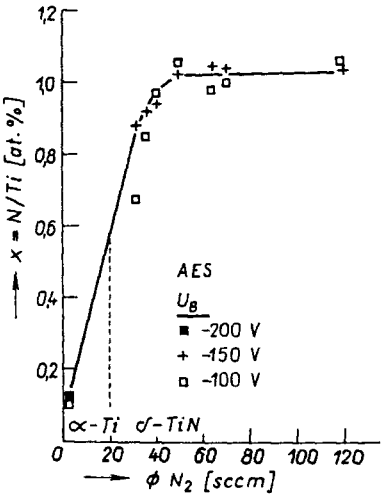

Fig. 6

Fig. 7 Texture coefficient TK in terms of reactive gas flowrate for a series of specimens deposited at bias U_B = -150 V.

Fig. 8 Texture coefficient TK_{111} for three different bias values used during deposition (U_B = -100 V, -150 V and 200 V) vs. reactive gas flowrate.

Fig. 9 Texture coefficients TK_{111}, TK_{200} and TK_{220} values vs. the current output of the magnetrons.

Fig. 10 Difference between the lattice parameters of compact TiN_x layers and those of separated layers vs. reactive gas flowrate for various deposition bias values.

Fig. 11 Difference between the lattice parameters of compact TiN_x layers and those of separated layers vs. the deposition bias on the substrate.

Fig. 12 Experimental values of lattice parameters for compact and separated TiN_x layers in terms of the magnetron current output at a constant partial nitrogen pressure.

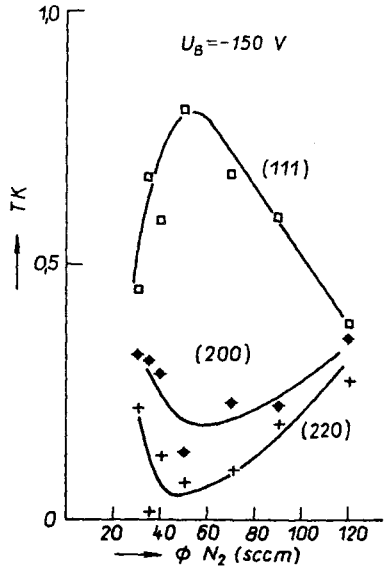

Fig. 7

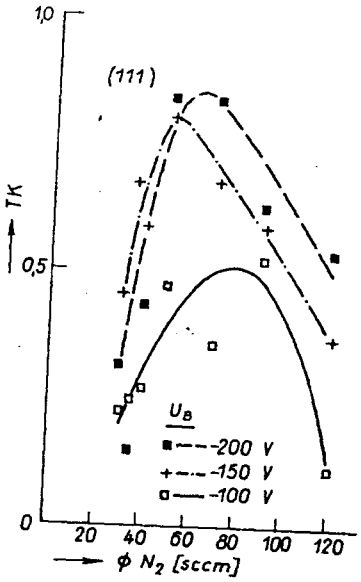

Fig. 8

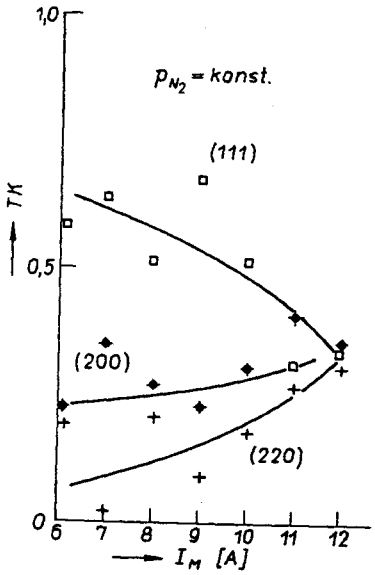

Fig. 9

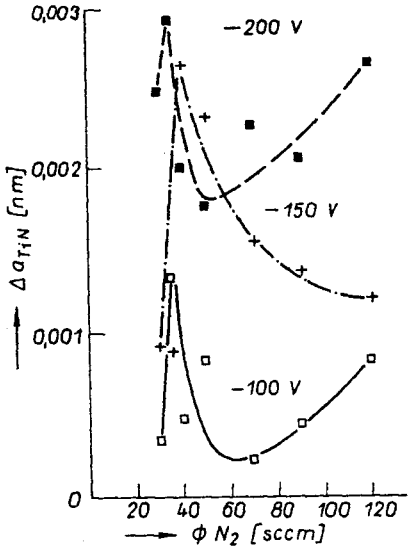

Fig. 10

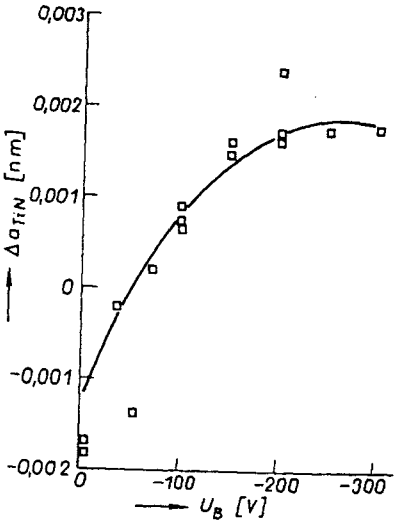

Fig. 11

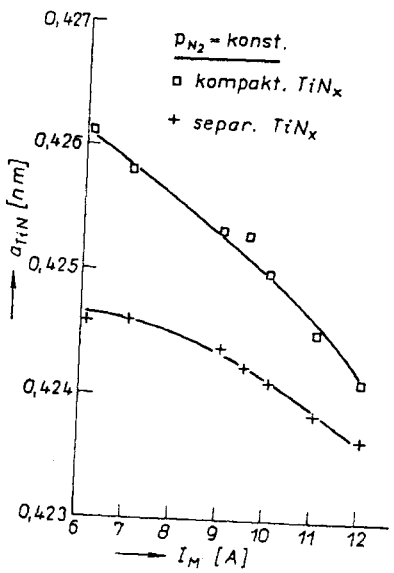

Fig. 12

Fig. 13 Adhesive force values for various bias values in terms of the nitrogen flowrate, established by the scratch test method.

Fig. 14 Durability of 6 mm dia. drills with TiN_x layers deposited at U_B = -150 V and at various reactive gas flowrates, evaluated at a feed s = 0.07 mm/rev.

KEY

1 Number of holes

Fig. 15 Durability of 6 mm dia. drills with TiN_x layers deposited at U_B = -150 V and at various reactive gas flowrates, evaluated at a feed s = 0.14 mm/rev.

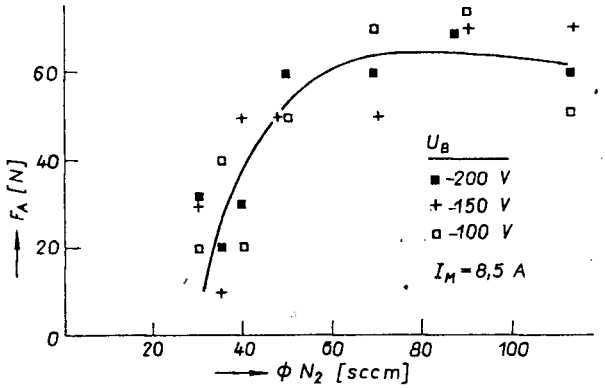

Fig. 13

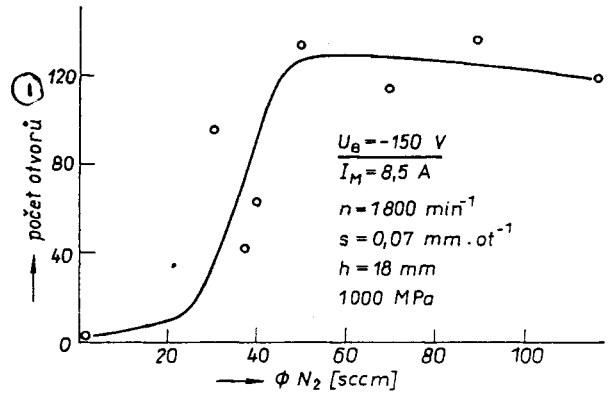

Fig. 14

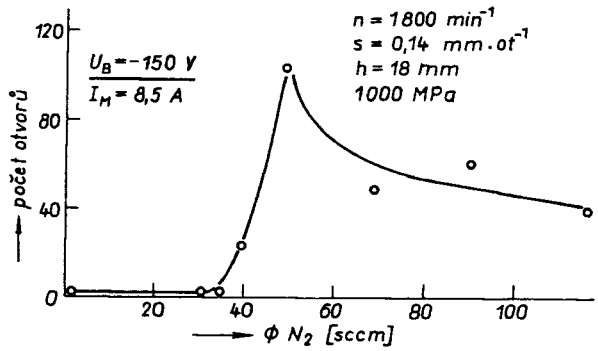

Fig. 15