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DEPOSITION OF DIAMOND-LIKE CARBON COATINGS BY UNBALANCED MAGNETRON SPUTTERING.

Edo Princen
Eindhoven, november 1994

Report nr. WPA: 110006

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ABSTRACT

Amorphous hydrogenated carbon films containing a small amount of metal (Me-C:H) have been deposited by closed field unbalanced magnetron sputtering. The films have graded compositions to optimise the adhesion to the substrates. Multilayer TiC/Ti-C:H films have also been deposited. The films have excellent properties: high microhardness (more than 2000 Hv), excellent adhesion to tool steel (a critical load of 100 N in the scratch test) and a coefficient of friction against bearing steel of about 0.1. The coating procedure, for in generally metals, is ideally suited to the system used. The graded film preparation is important for the intrinsic stress. The rather low deposition temperature (about 200 °C) has no influence on the properties of the metal substrate.
1 INTRODUCTION

The deposition of amorphous hydrogenated carbon films (Me:C-H) have been performed in a multiple magnetron coating system by the magnetron sputter ion plating technique. The apparatus is named the uniform deposition and plasma (UDP) system, and exists of a closed field unbalanced magnetron sputtering arrangement (PLASMAG).

The basis of the technique is that the outer magnets of the magnetron are made relatively much stronger, compared with the central magnet, than with the conventional magnetron. This can be done by placing more permanent magnets on the perimeter of the magnetron, or by simply weakening the central magnet. The several magnetrons are used to surround a central substrate, and adjacent magnetrons are manufactured with opposite polarities. The plasma is then confined within this closed field, preventing loss of electrons to the chamber walls and creating intense ion bombardment of the substrate.

The hybrid CVD/PVD process is controlled by a simple technique based on optical emission spectroscopy. An optical emission monitor is combined with a photomultiplier to monitor the intensity of the metal plasma in the neighbourhood of the target surface. A rapid response piezo-electric valve is then used to control the intensity of the plasma to a given level by an inlet of the reactive gas. The intensity setting gives the required stoichiometric composition of the compound being deposited. The intensive titanium line at 506 nm was selected as most suitable light emission of the plasma to control the process.[1]

The small amounts of metal in DLC have beneficial effects onto the compressive stress in the coating. A-C:H gives a rather high compressive stress, reducing the adhesion especially on steel. This is an essential reason for its limited practical application. Metal-containing hydrocarbon have much lower compressive stress than a-C:H. However, the wear resistance and friction coefficients are rather similar.[2]

Me-C:H can be prepared by reactive RF sputtering[4] or by reactive DC magnetron sputtering[6] in an argon-hydrocarbon gas mixture using metal targets. DC magnetron sputtering is somewhat difficult for films with low metal contents. It needs rather high reactive gas concentrations. Above a critical flow the target tends to be completely poisoned with a carbon film. The magnetron discharge becomes unstable. The deposition rate for DC is about one order of magnitude higher than RF magnetron sputtering and very promising with respect to industrial needs.

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The DLC film composes of a mixture of diamond, graphite and polymeric crystal structures. Diamond-like solids are often discussed together with crystalline diamond films even though their structure is significantly different (appendix B). The reason is that the diamond-like films exhibit a number of properties of bulk diamond. The diamond-like solids have very high densities compared with other conventional hydrocarbons and hydrocarbon polymers[3]. This high number density arises from their completely cross-linked structure and is another point of similarity with crystalline diamond.

The structure exists of SP³ coordinated carbon, tetrahedrally bonded to four other atoms, SP² carbon, trigonally bonded to three other atoms, and finally free bonds saturated by hydrogen atoms.

Diamond and graphite are two crystalline allotropes of carbon. In the diamond crystal structure each atom is covalently bonded to four other carbon atoms (SP³). Graphite is made up of layers of carbon atoms with strong trigonal bonds (SP²) in the basal plane. The fourth electron in the outer shell forms a weak Van der Waals bond between the planes, and accounts for such properties of graphite as lubricity, lower density, softness and a greyish black appearance.

In order to grow true diamond films, the SP³ type of tetrahedral carbon bonding must be exclusively maintained in a dynamic non-equilibrium system. It is now generally accepted that atomic hydrogen plays a crucial role in the promotion of SP³ bonding and for pure diamond deposition atomic hydrogen must be present. When carbon deposits tetrahedrally, each carbon atom on the growing face has a "swinging" bond and it is believed that these bonds are stabilised by the presence of atomic hydrogen. Also, if the carbon is tending to form a graphitic stucture, it can be broken up by energetic particle bombardment, since the SP² bonds are energetically less stable. The bombarding species may be hydrogen, oxygen, argon or any other ionised or energetic species.

The following figure shows schematically the structure.

Figure 2.1 Sketch of a representative compound model for amorphous hydrogenated carbon (a-C:H)

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Depending on the deposition method and parameters, the films may contain up to 50% hydrogen[7]. As a result of this structure, such amorphous diamond-like carbon films are more elastic than diamond.

Certain DLC films deposited by plasma-aided processes have extremely high internal compressive stresses and are extremely sensitive to microstructural disturbances. Even the slightest damage to the films may lead to spalling of large areas of the film. This, combined with the structure mismatch when DLC is applied to different kind of substrates, commonly leads to poor adhesion. In high mechanical stress applications, the adhesion of the films is often the critical factor.

Grading of very hard alloy nitride films through various intermediate compounds of different compositions has been shown to increase the scratch adhesions levels[1]. The interfaces ensure no abrupt changes in composition and the (compressive) stress is introduced gradually.

It has been found that the optimum film sequence in this case is:

Ti, TiN, TiCN, TiC, DLC.

It has also been subsequently found that the mechanical properties of the hard carbon films can be improved by incorporating a small percentage of metal dopant (usually ≈5% titanium)[1].

On the other hand is compressive stress necessary for diamond-like structure (SP³) formation in a hydrocarbon atmosphere[5]. The deposition mechanism is shown in the following figure.

\[ \text{H-H} \uparrow \]
\[ \text{compression} \]
\[ \text{C=C} \]

\[ (2.1) \]

\[ \text{C=C} \]
\[ \text{C=C} \]
\[ \text{C=C} \]

\[ (2.2) \]
3 EXPERIMENTAL DETAILS

The process used here for deposition of the carbon films (Me-C:H) is based upon a technique first reported by Dimigen and co-workers[4]. The introduction of a hydrocarbon gas (acetylene, butane) during sputtering causes a breakdown of the gas on the pure metal target surface so that the metal and hydrocarbon are sputtered simultaneously from the poisoned target surface. The amount of target poisoning by the hydrocarbon will determine for more than 90% the final composition of the DLC film. The other 10% structure is contributed by a plasma polymerization component[3]. If total poisoning of the metal target results, the process tends to become unstable owing to the non-conducting layer of carbon on the target surface, and "arcing" results.

A low RF power (13.56 Mhz) is often applied to the substrates to promote ion assistance during film deposition. In other words, the ion current density (ICD) to the substrates will be higher with RF bias voltage.

It is also possible to deposit a-C in a non-reactive mode. The graphite targets are conducting and therefore DC can again be applied to the magnetrons. The sputtered carbon is then deposited onto the workpieces with RF substrate bias without any hydrocarbon gas present.

The presence of the hydrocarbon gas will usually increase the deposition rate, but may affect the other properties due to the hydrogen concentration (see chapter 2).

Appendix C shows Teer’s standard DLC procedure.

The 'standard' DLC in production has the following configuration, minding different kind of DLC can be prepared. The coating looks the same, but many parameters can be changed (different bias voltage, deposition times, gases, other apparatus etc.)

![DLC layers diagram](image)

Fig. 3.1 A possible DLC coating for a substrate

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The several coatings were investigated by wear/friction test, ball cratering, scratch test, hardness-test and S.E.M.

The wear/friction test ("ball on disc test") is particularly valuable for the tribological behaviour. However, it is a first evaluation of a coating and in practice approval is still the one and only ultimate test.

Important factors with respect to the used wear-tester:

* air humidity plays an important role. Especially in the case of DLC. The reaction layer dependent on the environment determines the coefficient of friction and the wear rate. The relationship is often more or less like; low friction, high wear rate coatings in a dry environment and vice versa in a humid environment.

DLC forms a reaction layer in a tribological system under humid air conditions. This layer decreases the wear rate, but increases the coefficient of friction. It is in this case not anymore a pure graphitic friction like the dry air condition case. In the latter case is no formation of a reaction layer. This results in a lower coefficient of friction, but a higher wear rate of particularly the graphitic structure. Both coating-properties are of course also dependent on the share of diamond-like and polymeric structure. As a rule of thumb it can be concluded that the diamond-like structure is always beneficial for the coefficient of friction and the wear rate. This structure is non-reactive and very hard.

* the counterpart (=ball) is always bearing steel. Other materials could give opposite results.

* the contact area is circular, which is very unlikely in practice.

* the normal force is in the same direction as the gravity force. This introduces an unpleasant effect in the case of hard coatings. Abrasive particles could get stuck in the contact area. High wear rates are then very common, while another normal force direction shows less wear.

* the ratio of adhesive, ploughing or chemical wear is difficult to measure. This problem might be solved assuming the ploughing effect of friction will be present in the first rounds.

Ball cratering is a fast method to define the different layer thickness. In this experiment the coating is polished locally. A crater is made by rolling a ball, for several minutes, in a diamond paste on the same place. This method is for determining the layer thickness even better than the available S.E.M., because it is possible to distinct the different layers by colour.

Scratch testing (scratchtester ST 200) is a method to determine one of the most important factors of mechanical coatings, the adhesion strength to the substrate. Better known as the critical load.

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Optical investigation of not just the total failure load but also the area around the scratch gives even more information e.g. interface bonding, internal stress, failure mode (ductile or brittle) etc. Referring to the literature of Bull[9].

The hardness test (300 gr. Vickers) is mainly to check the brittleness of the coating. The absolute value has no sense, because the influence of the substrate is too big at a load of 300gr. and DLC is elastic!

The S.E.M. is a good mean to examine for the structure (columnar, dense, adhesion) and to determine the individual layer thickness. Figure 4.1 shows a S.E.M. picture of a DLC coating. It is possible to distinct two layers, a light and a dark one. The light layer has a columnar structure, the dark layer a dense structure.

Figure 4.1 S.E.M. picture of a DLC coating (6900 x)
5 RESULTS

The next combinations, compared to the 'standard DLC-procedure' (appendix C) have been investigated:

5.1 DLC without TiN interlayer

According to the publication of Ghosh and Kohler[8] the adhesion of TiCN on Ti is better than TiN on Ti (critical load resp. 60N and 50N). This apparent difference is tested in run numbers 8/22, 8/23 and 8/24 (runsheets at Teer Coatings Limited). The experimental results don't show any reasonable contrast between the two different interlayer structures in DLC. An explanation can be found in the fact that all the interlayers are related to each other. In the published report TiN and TiCN are tolayers. In DLC-coatings, TiN and TiCN are interlayers. The meaning of interlayers will be discussed further in this report.

5.2 DLC with niobium and titanium targets

Niobium is also a carbide-forming element. The difference between titanium, concerning sputtering, is the about 3/2 higher sputter rate in an argon atmosphere and the larger atom size than titanium. The unstable, relative big NbC (room temperature) could introduce compressive stress, necessary for the tetrahedral SP³ structure (chapter 2).

Samples of run 8/21 on toolsteel, produced with 1 Ti-target and 1 Nb target, showed very good tribological properties in comparison with standard DLC. In run-numbers 1 to 5, 2 Ti-targets and 1 Nb-target were used. One of the optimised coatings has the next properties.

COF against steel 0.1
critical load total failure 45 N; edge failure 15 N
No wear on counterpart after 1 hour 80 N wear-testing
Unfortunately, there was a leak in the Argon-pipe. Oxygen was in the chamber and it is well known that oxygen favours diamond growth.

The next remarks should be considered:

1) The scratchtest showed a lot of flaking. Probably because of the leak, causing contamination.

2) Wear and friction qualities are excellent, referring to the mentioned properties. This behaviour could be caused by a high SP³/SP² ratio.

3) An interesting property of Nb-C:H is the electrical conductivity. At an OEM reading of 10% (pure Ti) the DLC-layer is still conductive. This could be an

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advantage for electrical applications.

4) Because of economical aspects it should always be considered using niobium-targets instead of titanium-targets in order to get high ICD. Niobium-targets are 10 times more expensive than titanium-targets.

5.3 DLC without the gradually TiC interlayer

The DLC-toplayers deposited directly on the (hard) TiCN, thus without gradually TiC, don't show any bad adhesion in the scratchtest. Referring to figure 1 (App. A) showing a hard interlayer decreases the contact area but increases the stress as well as the shear stress[10]. It is this case I agree with the opinion of Prof. Arnell (Salford University, U.K.): "It seems that toughness for tribological applications is desirable and it may be worthwhile sacrificing some hardness to give significant increase in toughness". It can be concluded after inspection of scratches that the failure mode with the gradually TiC layer is less brittle[9], thus ideal for mechanical applications.

5.4 DLC without nitrogen in final stage

According to Palmier ea.[11] nitrogen favours a decrease of the internal stress level. This statement is not measurable with the available equipment. Personally I think it makes the coating brittle. Too high amounts of nitrogen might be a reason. After all I think the role of nitrogen is not enormous and it is just constrained to reactionlayer formation in frictioncases.

5.5 DLC with thinner TiN and TiCN interlayers

Although the interlayers are not a part of the contact area, they are very important for the stress level and failure mode in the coating. DLC, produced with standard procedure, exists of rather thick TiN and TiCN interlayers. Primarily to reduce the internal stress level in the coating and to improve the adhesion to the substrate. Depositing these layers thinner, there will be still a reduction of the stress level and the chance on failure (in the scratchtest) will be decreased.

The failure mode in a scratchtest can be made clear in figures 1 and 2 (App. A). The maximum shear stress occurs on the axis of symmetry at a distance 0.48r below the surface (r : radius of the contact area). Addition of a tangential traction has three effects. Firstly, the area of maximum shear stress moves forwards and towards the surface as the tangential force is increasing and will reach the surface at a friction coefficient of 0.3. Secondly, the region of tensile stress will develop in the surface at the back edge of the contact. Thirdly, the effect of the frictional traction is to add a compressive stress at the front edge of the contact and to
intensify the tensile stress at the back edge. Thus the region near the back edge of the contact is the most likely region of failure.[12]

The failure mode is often not at the interface coating/substrate, but in the coating (referring to pictures of Taiwanese Mr. Ma, figure 4). This is all assumable, because there is a tensile stress (figure 3) in the coating and a high shear stress. This combination of stresses accelerates failure. The high tensile and columnar structure in the TiN-layer causes often the first kind of this failure, because it is the weakest place. Thus thinner layers, less chance on failure!

Another important factor is the hardness of the interlayers. TiCN is relative hard. This causes a small contact area, introducing high stress levels (figure 5).

The sample with the rather thin (= 'soft') interlayers has after a scratchtest no failure at a load of 100 N. More investigation and optimisation will develop critical loads far above 100 N.

Depending on the application it is easy to control the flexibility of the coating by varying the thickness of the interlayers

5.6 DLC etching with argon ions (Ar⁺) after sputtering

The main reason of etching with Ar⁺ ions is to create SP³-bondings at a certain energy level (100eV). This will bring about lower COF and less wear[13]. The results are not measurable with the available equipment.

If there is any difference then it might be possible to do a 'multilayer etching-DLC' coating, hence the etching can penetrate a very small layer of a few Angstrom. For instance 5 minutes DLC... 5 minutes etching......5 minutes DLC......5 minutes etching etc.

The result will be a DLC-layer with more SP³-bondings, introducing a lower wear rate and a lower coefficient of friction.

5.7 DLC-coatings on cemented carbide inserts

TiC/Ti-C:H multilayers have been deposited on cemented carbide inserts. They will be tested in a micro-machining experiments. The several layers are produced by either gascontrolling or using carbon-targets. Appendix D shows the important parameters.
At this moment it is clear that role of the interlayers is important. In the past they didn’t get the attention they should deserve. Other important factors concerning DLC coatings are:

* A very thin unstoichiometric, softer TiN (less nitrogen) interlayer to exhibit ductility of the coating. The critical load in the scratch test will probably be higher.

* A microwave plasma instead of a RF glow discharge to get more stable process control. Above all it could be possible to sputter with less argon ions in a microwave plasma. By exciting the hydrocarbons with the proper frequency it might be possible to maintain a plasma with C⁺ ions (“self-sputtering”), favouring a higher ion current density to the substrate.

* It is generally known that the amount of hydrogen in DLC is a very important factor in resulting the ratio SP³/SP² (see chapter 2). Even more important than the amount of hydrogen is the form of hydrogen in DLC.[3] The hydrogen can be unbonded, bonded in SP³ structure or bonded in SP² structure. The kind of bonding has influence on the coating properties.

* There might be a relationship between high ion current density and diamond-like carbon growth. This is not measurable with the available equipment. SEM investigation of Nb-C:H, produced by high ICD, showing a very dense structure confirms this statement. More investigation is definitely necessary.

* In the past lots of studies have been done on the influences of gases on diamond growth. At this moment it is clear that the presence of even small amounts of certain gases can affect the process, e.g. a leak. After comparing the different processes (CVD,PVD,IBAM etc.) of diamond-growth and their relationship with gases. It is very difficult to define relations, because a gas property depends on temperature and pressure. More investigation is certainly necessary, especially in combination with the kind of powersupply (RF, DC, microwave).

* By varying the thickness and hardness of interlayers it is possible to determine some very important properties of a coating in general. The message from this work is that interlayers can be useful in enhancing adhesion, but their structure should be dictated by the requirements of the application.
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12 Arnell, unpublished work.

Fig. 1: Iso-stress levels in substrate under normal load.
Fig. 2: Iso-stress levels under normal and tangential load ($\mu=0.3$)
Fig. 3: Stress in coating under normal point-load.

Fig. 4: Coating failure in the coating.
Fig. 5:
a contact area of DLC with \textit{soft} interlayer (load F).
b contact area of DLC with \textit{hard} interlayer (load F).
### Table: Properties of Diamond and DLC Materials (from literature)

<table>
<thead>
<tr>
<th>Property</th>
<th>Thin Film</th>
<th>Bulk</th>
</tr>
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<tr>
<td>Crystal Structure</td>
<td>CVD Dia</td>
<td>a-C</td>
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<tr>
<td></td>
<td>Cubic</td>
<td>Amorphous</td>
</tr>
<tr>
<td></td>
<td>$a_0 = 3.561 \text{Å}$</td>
<td>$\text{mixed }\text{sp}^3 \text{ and }\text{sp}^3/\text{sp}^2 \text{ bonds}$</td>
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<tr>
<td>Form</td>
<td>Facteted crystals</td>
<td>Smooth to rough</td>
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<td>1,200-3,000</td>
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<td>Density</td>
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<td>1.6-2.2</td>
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<tr>
<td>Refractive Index</td>
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<td>1.6-3.1</td>
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<tr>
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<td>$&gt;10^{10}$</td>
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<td>Hydrogen Content (H/C)</td>
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<td>Growth Rate (µm/h)</td>
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<td>2</td>
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<td>(synthetic)</td>
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APPENDIX C

OUTLINE OF A DEPOSITION PROCEDURE FOR Ti-C:H.

1. Pump to 5 * E-5 Torr
2. Cooling-water on + leaktest
3. Check the nitrogen pressure of 3.5 * E-4 Torr with the needle valve. Read the value and close the valve
4. Input argon 3 * E-3 Torr. This pressure needs to be constant during the run.
5. 30 minutes cleaning with 2 Ti-targets on 0.2A (ramp)
   DC substrate bias -1000V
   RF substrate bias 200W forward power
6. 3-4 minutes pure Ti (2 targets 6A each)
   DC substrate bias -250V
   RF substrate bias -100V DC-bias
7. 20 minutes TiN with nitrogen through the piezo valve.
   55% OEM of pure titanium
8. Gradually input of extra nitrogen through the needle valve, see step 3. Inlet of nitrogen to 3.5 * E-4 Torr.
9. 30 minutes TiCN with acetylene (or butane) through the piezo valve. 50% OEM of pure titanium.
10. Gradually decreasing of the OEM reading from 50% to 15% in about 20 minutes.
    The deposited layer is unstochiometric TiC.
12. Leave the system until the desired DLC thickness is reached (about 40 minutes).

It is necessary to clean the targets after each DLC-run for about 45 minutes with a current of 6A.

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DEPOSITION OF TiC/Ti-C:H MULTILAYERS

Multilayers can be deposited by:

GAS PULSING: x min. OEM 50% ... x min. OEM 15% .... etc.
-fine or thick multilayers with diffuse interfaces

SEQUENTIAL DEPOSITION
-thick layers

SIMULTANEOUS DEPOSITION: it is possible to deposit a-C with an extra carbon target and TiC with the presence of a hydrocarbon gas. Non-continuous sample rotation is recommended.
-fine multilayers with discrete interfaces

GAS PULSING AND SHUTTERING: the target is covered during switching over of the OEM-reading
-fine multilayers with discrete interfaces
## DLC COMPOSITION ON CEMENTED CARBIDE INSERTS

<table>
<thead>
<tr>
<th>Run Number</th>
<th>GAS 1</th>
<th>GAS 2</th>
<th>GAS 3</th>
<th>TARGETS</th>
<th>bias power</th>
<th>Ti [W]</th>
<th>time [min.]</th>
<th>TiN [W]</th>
<th>time [min.]</th>
<th>OEM [%]</th>
<th>TiCN [W]</th>
<th>time [min.]</th>
<th>OEM [%]</th>
<th>DLC [W]</th>
<th>time [min.]</th>
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<td>2</td>
<td>Ar</td>
<td>N₂</td>
<td>C₄H₁₀</td>
<td>2 Ti</td>
<td>DC-6 Amps</td>
<td>RF</td>
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<td>20</td>
<td>25</td>
<td>55</td>
<td>20</td>
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<td>3</td>
<td>Ar</td>
<td>N₂</td>
<td>C₄H₁₀</td>
<td>2 Ti</td>
<td>DC-6 Amps</td>
<td>RF</td>
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<td>4</td>
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<td>1 Ti+ 1 C</td>
<td>DC-6/1 Amps</td>
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<td>Ar</td>
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<td>1 Ti+ 1 C</td>
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<td>17</td>
<td>45</td>
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<td>20²</td>
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</table>

¹) 5 minutes 50% and 5 minutes 15%, varying for 70 minutes.
²) with gradually TiC-layer; in 20 min. from 45% to 10%.

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